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THE ACTION OF CARBON DIOXIDE ON THE BORATES OF BARIUM.

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In Volume 10 of THIS JOURNAL, one of us, with W. M. Burton, published a method for the separation and determination of boric acid. The proposed procedure was as follows: If the acid is in solution, the liquid containing it is made slightly alkaline with caustic potash and evaporated in a porcelain dish to a volume of 10 or 12 cc. If, on the other hand, the material is insoluble, *e. g.* a silicate, about 4 grams of solid potassium hydroxide are fused in a nickel crucible until the liquid mass becomes tranquil. After cooling and solidifying, the pulverized mineral is spread over the surface, and the crucible is heated for two hours just high enough to keep the hydroxide in molten condition, the contents being stirred from time to time with a stout platinum wire, which is allowed to remain in the crucible. The soluble matter is separated from the insoluble by extraction with water, filtration, and washing upon the filter. The filtrate is then evaporated to the small volume mentioned above. If the mineral contains iron, the contents of the crucible are treated with not less than 400 cc. of water, and heated for some time in order to insure

the precipitation of all of the ferric hydroxide. The filtrate is then evaporated as in other cases.

The solution of alkaline borate is treated with tropæolin (better with methyl orange), and then, under a covering glass, with sulphuric acid until an acid reaction is obtained. The covering glass is washed into the dish, and the liquid cautiously brought to the neutral condition with very dilute caustic potash. The solution, which contains in the free state only boric, carbonic, and silicic acids, and whose volume should not exceed 20 cc., is dried by stirring into it anhydrous copper sulphate. The pulverized dry material is transferred to a straight calcium chloride tube, in the bottom of which a plug of cotton wool has been placed, and extracted with absolute alcohol.

In this manner it was found practicable effectually to separate boric acid from the bases and acids with which it is usually associated, and this was regarded by the authors of the process as the most, and in fact the only, important feature of their contribution. When the question of determining the acid in the alcoholic solution arose, they were confronted with the well-known difficulties of the methods at that time available for getting boric acid in solution into weighable form. The procedure which they adopted was free from some of the objections to earlier processes, and gave, as far as it was tested, very satisfactory results. It was as follows: The alcoholic extract was drawn from the filter into a flask containing a measured volume of a standard solution of barium hydroxide. The excess of the hydroxide was converted into carbonate by passing a current of carbon dioxide through the liquid. The contents of the flask were then transferred to a weighed platinum dish, evaporated to dryness, and heated to constant weight by rapidly moving the flame of a triple burner over the outer surface of the dish. Knowing the weight of the barium in the mixture of salts, and that of its carbonate, if all of it were precipitated by the carbon dioxide, the weight of the boric acid could be calculated by the following proportion:

Mol. wt. B_2O_3—mol. wt. CO_2 : mol. wt. B_2O_3 : :
wt. found—theoretical wt. $BaCO_3$: wt. B_2O_3.

The essential weakness of basing the estimation of the acid, after its separation, upon such a calculation is perfectly obvious, and the fact that analytical errors are magnified threefold in the results was not overlooked by the authors of the process. It was believed, however, that with careful work quite as high a degree of accuracy could be attained by this method as by the others then in use.

The process was tested by its authors by determining the boric acid in three substances: borax glass, datholite from Bergen Hill, and tourmaline from Pierrepont. It was then placed in the hands of two of the best analysts in the laboratory, with the request that they also try it upon some of the same materials. All of the results were satisfactory.

In Volume V (series 4) of the American Journal of Science, L. C. Jones describes some experiments with an aqueous solution of boric acid which was treated with an excess of barium hydroxide, then with carbon dioxide, and afterwards dried, and the residue heated with a view to securing constant weight. The results exhibit great lack of uniformity, and differ very widely in nearly every case—sometimes in one direction and again in the other—from the quantities which should have been obtained if the residues consisted only of the metaborate and carbonate of barium. The author concludes that the weights vary with the degree of the ignition; and this he supposes to be due to the action of the carbon dioxide upon the metaborate, as well as upon the excess of hydroxide. His view appears to be that carbon dioxide precipitates a portion of the barium from the metaborate, liberating boric acid which is lost, in part, during the subsequent evaporation. On igniting the residue afterwards, the portion of free acid which was not lost during the evaporation displaces carbon dioxide with reformation of barium borate, and the net result must be positive or negative according to the degree of the completeness of this reaction. If all of the free acid is reconverted into metaborate, there should be a deficit just equal to the weight of the boric acid which was lost during evaporation. Again, on fusing together weighed quantities of barium metaborate and carbonate, it was found that the prod-

uct weighed less than the original mixture, showing that the two salts react with liberation of carbon dioxide.

"These results," the author says, "were so surprising in the light of the experience of Morse and Burton that the question of the possibility of breaking up by carbon dioxide the barium metaborate already formed was put to the test directly." Accordingly, he prepared a known weight of the salt, dissolved it in hot water, passed carbon dioxide through the solution, evaporated to dryness, ignited, and weighed. There was an increase in weight, showing "that carbon dioxide had been absorbed, while a corresponding amount of boric acid had not been volatilized." "After passing in carbon dioxide and igniting, the increase in weight was 0.028 gram representing the gas absorbed less the boric acid volatilized."

Thinking that possibly the amount of the carbon dioxide might be so regulated "as to leave the metaborate practically unattacked.... carbon dioxide was passed above the stirred solution until no further precipitate formed upon the surface, the barium present being in excess of that required to form a metaborate." On ignition an apparent loss of 0.0412 gram of boric acid was observed. Concerning this experiment, the author says: "The variation of this result from the theory shows that under these conditions the metaborate is not unaffected by the carbon dioxide, *the loss being due, of course, to the escape of boric acid.*" In the succeeding experiment phenolphthalein was added to a solution of boric acid which had been treated with an excess of barium hydroxide, and the current of carbon dioxide was discontinued when the color disappeared. The dried residue was repeatedly ignited, with the result that the apparent error varied between +0.0438 gram after the first heating, and —0.013 gram after the seventh. Finally, it was proved that, by continuously removing the boric acid in the form of the methyl ether, the metaborate of barium can be completely decomposed by carbonic acid.

Near the beginning of his article, after giving a synopsis of the method proposed by Morse and Burton, the author says: "I have made a study of this method applied to pure boric acid, but have been unable to obtain results similar to

those of Morse and Burton." At the close, he adds: "In view of the facts which I have described, it is difficult to see under what conditions Morse and Burton prevented the excessive action of carbon dioxide and obtained in their analytical method the excellent results which they record."

We must question the correctness of the author's statement, that h has "made a study of this method;" for he appears to us to have failed to satisfy the first requirement of a genuine study of the same, in that he has neglected to adhere to the essential conditions under which the original work was done. He employed *aqueous solutions* only, and yet seems to assume that he was dealing with the meta salt, notwithstanding the presence of an excess of barium hydroxide, whereas it is highly probable that a compound containing a larger proportion of the base was formed. An experiment which may be cited as evidence to this effect is recorded by P. Berg,[1] who found that when barium hydroxide is added to an aqueous solution of boric acid in such quantity that the ratio of BaO to B_2O_3 is as 1.5 to 1, the precipitate which is first formed is dissolved, and that, too, by virtue of the additional half molecule of BaO.

On the other hand, the authors of the method in question worked with *strong alcoholic solutions* and, therefore, were dealing, without doubt, with the metaborate; since it has been shown by Berg[2] that in alcoholic solutions the meta salt is precipitated, whether the ratio of B_2O_3 to BaO is as 1 : 1, 1 : 1.5, 1 : 2, 1 : 3, or 1 : 3.5.

Again, in the aqueous solutions containing an excess of barium hydroxide, *i. e.*, more than is required for the formation of the meta salt, the borates (whatever their composition may have been) must have been to a great extent dissolved, in which condition they would be acted upon rapidly by the carbon dioxide; while in the strong alcoholic solutions employed by Morse and Burton, the metaborate is only very slightly soluble. The great mass of the salt was therefore in a condition in which it could be acted upon only slowly by the gas. According to their original directions, the volume of the

[1] Ztschr. anal. Chem., **16**, 26.
[2] *Loc. cit.*, 27.

aqueous solution of barium hydroxide which is employed in a determination of boric acid is about 25 cc. Into this is drawn the solution of boric acid in absolute alcohol, which, together with the alcohol used in washing, has a volume of from 90–100 cc. Hence the liquid which is afterwards treated with carbon dioxide for the purpose of precipitating the barium from the excess of hydroxide is—roughly estimated—at least a 78 per cent alcohol. The solubility of the metaborate in a 75 per cent alcohol is given as 1 part in 55,000. 125 cc. of the 78 per cent liquid should not, therefore, contain more than 2 mgms. of the metaborate in solution when treated with carbon dioxide, and even this small quantity should not be attacked by the gas until after the excess of the hydroxide has been neutralized. At all events, it seems highly improbable that the undissolved metaborate should be seriously attacked by the carbon dioxide during the short time required to neutralize the excess of hydroxide. If the treatment with the gas were carried beyond the neutralization of the hydroxide, the metaborate would doubtless suffer to some extent; but the immediate result would not be, as supposed by Jones, the liberation of boric acid, but rather the formation of a still more acid borate. He speaks repeatedly of the *liberation* of boric acid when carbon dioxide is passed into a solution of the metaborate of barium, and ascribes certain considerable deficits in weight to a loss of this free acid during evaporation. But one of his own experiments appears to indicate that the product of the action of the gas upon a borate is a more acid salt and not the free acid; for he states that when he passed carbon dioxide into a solution containing 1 gram of boric acid and 0.15 gram of barium hydroxide, "no precipitate could be obtained." This must mean that carbon dioxide is incapable, under the conditions, of decomposing the most acid of the borates.

An evaporating solution containing, as some of those of the author probably did, a very acid borate of barium, the acid carbonate of the same, and perhaps free carbonic acid, quickly loses the free and semicombined carbonic acid, and this loss should be attended by the simultaneous formation of a borate holding in combination a larger proportion of barium. If, as

he supposes, these solutions also contain free boric acid, and, as he states, "the division of the base between boric acid and carbonic acid falls under the principle of mass action," the rapid loss of the latter during evaporation should be followed by an equally rapid neutralization of the former. Hence, even if some of the boric acid is actually in the free state, at the beginning of the evaporation, it cannot long remain free, but must recombine with the barium as the equilibrium is disturbed by the disappearance of the carbonic acid; and the acid borates thus formed, though possibly not wholly stable, should not lose acid during evaporation as readily as does an aqueous solution of boric acid in the absence of a base. It is difficult for us to understand, in view of "the principle of mass action," how any of the boric acid should be actually liberated until all of the barium carbonate had been converted into the acid salt. This, however, would involve very prolonged treatment with the gas.

These considerations led us to think that Jones, in ascribing certain deficits in weight to loss of boric acid by volatilization, had misinterpreted the cause of the results which seemed to him so strange. It appeared to us improbable that, under the conditions, any weighable quantity of the acid could be lost in that way. On the other hand, the following simple hypothesis, which is based on well-known facts, would account for all the phenomena observed by him.

1. Having treated his boric acid in aqueous solutions with an excess of barium hydroxide (*i. e.* more than was necessary to form the meta salt) he had to deal, not as he appears to suppose, with the metaborate, but with a salt containing a larger proportion of the base—possibly with $(BaO)_3B_2O_3$.

2. On conducting carbon dioxide into the liquid, any excess of hydroxide would be neutralized, and then the borate would be attacked with precipitation of barium carbonate and formation of an acid borate; and whether a mixture of neutral and acid borates, or the metaborate, or possibly a still more acid salt would be produced, would depend on the length of the exposure to the gas, as would, likewise, the initial weight of the dried residue. If the treatment with carbon dioxide were stopped before all of the neutral borate had been

converted into the meta salt, the residue would be too light—that is, for a mixture of carbonate and metaborate; if it were carried just to this point (which would happen only by chance), the expected weight would be obtained, while any more prolonged action of the gas would give a residue having too great a weight.[1]

3. On heating the residue to a temperature sufficiently high, the acid borates—the metaborate as well as the more acid salts—would attack the carbonate with formation of less acid borates and expulsion of carbon dioxide. This reaction—with the consequent decline in weight—would continue until all of the acid had been converted into the neutral—or most basic—borate of barium, when the weight would become constant.

The decomposition of carbonates by acid borates at high temperatures is, of course, a very familiar reaction; and it affords the most obvious explanation of the continuous loss in weight which was observed by Jones when he subjected his mixtures of borate and carbonate to repeated ignitions. That the metaborate will decompose the carbonate of barium was shown by one of Jones's own experiments. The assumption that any portion of the deficits in weight was due to loss of boric acid by volatilization appears to be unnecessary.

He is clear, both as to the fact that carbon dioxide decomposes the meta salt in aqueous solution, and that the metaborate decomposes the carbonate of barium at high temperatures; but his evident conviction that his solutions, before treatment with carbon dioxide, contained the metaborate, despite the excess of barium hydroxide, and, therefore, that his conditions were comparable with those of Morse and Burton, is, we believe, without justification. If they contained a more basic borate, as it is morally certain they did, it is obvious that Jones could not have obtained the expected weight except by accident. He had two chances of obtaining a residue consisting of metaborate and carbonate only: first,

[1] It is to be remarked in this connection, however, that a too great initial weight of the residue does not necessarily indicate that the action of the carbon dioxide has gone beyond the formation of the metaborate, *i. e.*, has resulted in the production of a still more acid salt; since the metaborate, when formed in the presence of water, is hydrated, and the first heating of the residue may not suffice for its complete dehydration.

to stop the treatment with carbon dioxide when his more basic salt had been converted into the metaborate; second, having passed beyond this point, to discontinue the subsequent ignition when the more acid borate had been reconverted into the meta salt at the expense of the carbonate. There is, however, no possible means of determining when either of these goals has been reached. That phenolphthalein will not serve for the identification of the first is clear from Jones's experiment No. VII, where, on the first weighing, a surplus of 0.0438 gram was obtained, notwithstanding the fact that "the current of gas was stopped when the color of the indicator disappeared."

It may be urged that even if Morse and Burton had the metaborate in insoluble condition, and it had not been sensibly attacked during the treatment with carbon dioxide, nevertheless, in the subsequent attempt to heat the dried residue to constant weight, the metaborate must have attacked the carbonate. It has since then come to light that some caution must be exercised in this part of the manipulation. In the original description of the method, it was simply stated that the residue was heated to constant weight over a triple burner. The practice then, and on the few occasions when the process has since been used, was to hold the burner in the hand and rapidly play the flame over the platinum dish in order to secure as uniform a temperature of the contents as possible. The object in using a triple burner was not to obtain a very high temperature, which is not necessary, but, rather, to employ a flame large enough to keep the whole dish hot. No difficulty was experienced, when the heating was conducted in this manner, in quickly obtaining constant and correct weights. Nevertheless, it must be admitted, the authors of the method did not at that time suppose that the temperature at which the meta salt will attack the carbonate is so low as it has since been found to be. The temperatures employed by Jones were evidently far above those to which Morse and Burton heated their mixtures of metaborate and carbonate.

The authors of the present paper proposed at the outset to undertake a somewhat elaborate investigation of the action of carbonic acid on the borates of barium under different condi-

tions, and of the action of the acid borates upon the carbonate of barium at high temperatures. In the midst of the work, however, the laboratory in which the investigation was in progress, also all of the materials and apparatus employed in connection therewith, were destroyed by fire, compelling them to postpone for a considerable time the further prosecution of the work in this direction. Enough, nevertheless, had been accomplished to justify certain conclusions, and we give our results now, notwithstanding the incompleteness of the investigation, because we were originally delayed in taking it up far beyond the time when the communication of Jones should have received attention.

The first question which we undertook to examine bears upon the method of Morse and Burton. It is possible, if the alcoholic liquid containing the insoluble metaborate and the excess of the hydroxide of barium is treated with carbon dioxide much longer than is necessary for the neutralization of the latter, that a sensible quantity of the boric acid might be lost in the form of ethyl borate during the subsequent evaporation. We determined to test this point under much severer conditions than those which prevail when the process is carried out according to the original directions. To this end a solution of crystallized boric acid in absolute alcohol (1 cc. containing 0.007 gram B_2O_3) and an aqueous solution of barium hydroxide (1 cc. containing 0.0224 gram BaO) were made. A tubulated retort, with its neck near the small end bent to an angle and raised somewhat above the horizontal, was attached to a condenser. The glass stopper was replaced by a cork carrying a tube for the introduction of gas. Measured quantities of the solutions of acid and hydroxide and an additional quantity of alcohol were brought together in the retort and treated for a considerable time with carbon dioxide; and then, without interrupting the current of gas, the alcohol was distilled off and the distillate tested by the flame reaction for boric acid. More alcohol was added to the residue in the retort and distilled off as before, the treatment with carbon dioxide being continued throughout the time occupied in the distillation. This retreatment of the residue with alcohol with subsequent distillation in a current of carbon dioxide was

three times repeated with each mixture. Previously we had determined what, for us, was the lower limit of the flame reaction for boric acid, and had found that we could just discern the green color when 1 part of the acid was dissolved in about 14,200 parts of absolute alcohol. The results of four experiments of the kind described are given below. The letters *a*, *b*, *c*, and *d* signify 1st, 2nd, 3rd, and 4th distillations:

		Volume of distillate. cc.	Concentration of distillate. Per cent.	Character of flame reaction.
I.	*a*	....	72.0	negative
	b	....	82.0	"
	c	....	92.0	traces
	d	....	96.0	"
II.	*a*	52.0	68.0	negative
	b	50.0	64.5	"
	c	54.0	68.0	"
	d	52.0	....	"
III.	*a*	50.5	75.6	negative
	b	52.0	74.6	"
	c	51.1	72.6	"
	d	50.5	....	"
IV.	*a*	51.0	74.0	negative
	b	51.5	69.5	"
	c	53.0	64.5	"
	d	51.0	71.0	"
V.	*a*	51.2	75.0	negative
	b	51.2	73.0	"
	c	51.2	74.0	doubtful
	d	50.9	72.0	"

In experiments I. to IV. portions of the distillates were burned directly, and it will be noted that only when the alcoholic concentration rose to 92 per cent, or higher, did the distillates contain a quantity of boric acid which could be detected by the flame when the test is thus applied. In experiment V., on the other hand, the distillates which gave no green flame when burned were treated with a small quantity of caustic potash and evaporated to dryness, and the flame test was then applied to the residues after treating them with 0.5 cc. of absolute alcohol and a little concentrated sulphuric acid.

The quantities of boric acid which were carried over appear to have been very minute, notwithstanding the distillation in

a current of carbon dioxide; and this fact renders it probable that a loss of acid in consequence of etherification is not to be feared when the evaporation is carried out in the manner prescribed by Morse and Burton; that is, in the absence of the gas and only after a moderate treatment with it. Nevertheless, it was our intention to return to the subject at a later period for the purpose of securing positive evidence upon this point.

In one of Jones's experiments, boric acid was treated with an excess of barium hydroxide (*i. e.* with more than enough to form the metaborate), and the mixture with carbon dioxide until no further precipitate formed on the surface of the stirred liquid. The weight fell short 0.0412 gram, "the loss being due, of course, to the escape of boric acid," the author says. As we have already explained, such a loss of the acid by volatilization seemed to us improbable under the conditions. A better explanation of the deficit appeared to be that Jones either had not carried the treatment with carbon dioxide far enough to convert all of his more basic borate into the meta salt; or, having carried it to this point or beyond, that he had afterwards heated the material so high that a more basic salt than the metaborate had been formed at the expense of the carbonate. We therefore undertook to ascertain whether, under conditions analogous to those described by Jones, there is an appreciable loss of boric acid.

Accordingly, some powdered turmeric root was extracted, first with water and then with 95 per cent alcohol, and from the alcoholic extract test-papers were prepared which were afterwards properly protected from the light.

Aqueous solutions containing minute known quantities of boric acid were tested with the papers with a view to determining the limit of the reaction, the solutions having first been treated with just enough hydrochloric acid to produce a distinct acid reaction with methyl orange. When a test was to be made, an equally dilute solution of hydrochloric acid in pure water was employed for comparison. A paper was cut in halves, one half was dipped in the acidified solution of boric acid, and the other for the same length of time in the dilute hydrochloric acid. Both strips were then dried upon a

warmed glass plate and the effects compared. When a paper failed to show the reaction after the first dipping and drying, it was redipped and dried again and again. In this way a distinct reaction could be obtained in solutions so dilute that a single treatment failed to reveal a trace of acid. The coloring-matter, however, gradually concentrated in the highest part of the wet portion of the strip rendering an indefinite repetition of the process impracticable. In this way we were able to detect 1 part of the acid in 59,000 parts of water by a single dipping, and 1 part in 143,000 by dipping four or five times. The turmeric test for boric acid in water appears, therefore, to be much more delicate than that of the flame in alcoholic solutions.

In the following group of experiments, the same apparatus was employed as before, but the current of carbon dioxide, which in the earlier experiments had been conducted through the retort during the evaporation, was replaced by one of heated air. This was done in order to facilitate the evaporation upon the water-bath. An aqueous solution of boric acid containing 0.00636 gram B_2O_3 per cc., and one of barium hydroxide containing 0.02538 gram BaO per cc., were brought together in the retort, the latter being in excess of the quantity required to form the metaborate. Phenolphthalein was added and carbon dioxide conducted through the liquid for a short time longer than was necessary to destroy the color. The current of carbon dioxide was then replaced by one of air, which was heated before entering the retort by passing it through a hot porcelain tube filled with fragments of the same material. In this way a comparatively rapid distillation could be effected upon the water-bath. The whole of the water was distilled out of the retort and collected in the receiver. The conditions and results are stated below :

	Volume of liquid in the retort.	Ratio of $BaO : B_2O_3$.	Number of times necessary to dip paper to detect acid.	Possible amount of B_2O_3 in the distillate.
	cc.			Gram.
VI.	13.77	2 : 1	3	0.00012
VII.	14.84	2 : 1	3–5	0.00013
VIII.	14.36	2 : 1	3	0.00013
IX.	14.72	2 : 1	4	0.00010
X.	22.35	4 : 1	4	0.00016

It is assumed, in making the estimates given in the last column, that since 1 part of the acid can be detected in 59,000 parts of water by once dipping, and 1 part in 143,000 parts by dipping four times, 1 part in 87,000, and 1 part in 115,000 could be detected by dipping twice and three times, respectively.

The quantity of boric acid found in the distillates is so minute that one may well question whether we have not to do here with a mechanical transportation of the finely divided liquid in suspension above a mass of liquid through which a gas is breaking its way.

Three similar experiments (Nos. XI., XII., and XIII.) were made with alcoholic solutions, but the work in this direction was not completed for the reason already explained. An alcoholic solution of boric acid and a water solution of barium hydroxide were introduced into the retort, and enough alcohol added to bring the concentration of the whole up to 50 per cent. As before, the mixture was treated with a little phenolphthalein, then with carbon dioxide, and finally distilled to dryness with the aid of a current of hot air. The distillate was tested in the manner previously described with turmeric paper. The attempt to determine the limit of sensibility of the reaction in alcoholic solutions was unfinished; but it appeared probable, from the few experiments which were made, that a smaller amount of boric acid can be detected in 50 per cent alcohol by the turmeric test than can be found in absolute alcohol by the flame reaction. The dipping of the papers, however, cannot be repeated as many times in an alcoholic, as in an aqueous, solution, owing to the solubility of the coloring-matter in the former.

	Volume of liquid in the retort. cc.	Ratio of $BaO : B_2O_3$.	Number of times necessary to dip paper to get reaction.
XI.	15.75	2 : 1	3
XII.	31.48	2 : 1	2
XIII.	24.48	4 : 1	2

In the second part of our work, we proposed to study the effect of different temperatures upon the weights of mixtures of borates and carbonate, such as are produced when boric

acid is treated with an excess of barium hydroxide and afterwards, more or less thoroughly, with carbon dioxide; and to determine also the effect of exposing these mixtures, after heating, in an atmosphere containing carbon dioxide. It was to be expected, in view of the known conduct of other similar mixtures, that, if the more acid borates (including the meta salt) decompose the carbonate at high temperatures, at lower temperatures the gas would be reabsorbed, and that certain ranges of temperature might be found through which acid borates of definite composition would be stable, notwithstanding the presence of barium carbonate or of carbon dioxide. As far as the matter in controversy is concerned, it was our object to find the temperature at which it was presumed a mixture of the metaborate and the carbonate of barium is stable, or, rather, the temperature at which it becomes unstable.

Solutions of boric acid in alcohol and of barium hydroxide in water were employed, the latter being always in excess of the quantity required to form the meta salt. The character of the treatment with carbon dioxide is described in connection with each experiment.

Experiment XIV.

Weight of $BaO = 0.2745$ gram $= 0.35315$ gram $BaCO_3$.

" " $B_2O_3 = 0.09834$ gram $= 0.17418$ gram H_3BO_3.

$= 0.12362$ gram $HBO_2 = 0.31419$ gram $BaO.B_2O_3$.

Excess of $BaO = 0.0586$ gram $= 0.07547$ gram $BaCO_3$.

Weight of mixture, if consisting of $BaO.B_2O_3$ and $BaCO_3$ only, $= 0.38959$ gram.

Volume of the mixed solutions $= 42.24$ cc.

The material was evaporated to dryness on a water-bath under an uninterrupted current of carbon dioxide.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of BaO. B_2O_3 + $BaCO_3$. Gram.
1. Dried 1½ hours on water-bath	0.44427	.....	+0.05468
2. Exposed cold, after moistening, to CO_2 for 48 hours, and then heated on water-bath	0.44426	0.0000	+0.05468
3. Heated 40 minutes over triple burner	0.38591	—0.05835	—0.00368
4. Heated 40 minutes over triple burner	0.37699	—0.00892	—0.01260
5. Heated 15 minutes over triple burner	0.37428	—0.00271	—0.01531
6. Heated 15 minutes over triple burner	0.37278	—0.00150	—0.01581
7. Heated 15 minutes over triple burner	0.37152	—0.00126	—0.01807
8. Heated 5 minutes over triple burner	0.37031	—0.00121	—0.01928

The results recorded above are similar to some of those obtained by Jones. The weights in the beginning are greater than those calculated for a mixture of carbonate and metaborate only, but on successive strong ignitions they decline, rapidly at first, and then more slowly. The excess of weight observed when the residue was heated only to the temperature of the water-bath shows one of two things: 1. That the metaborate, if it was formed at all, had been robbed of some of its barium by the carbon dioxide with formation of a more acid salt; or, 2. That the metaborate took up and retained water of crystallization at the temperature of the bath. If the residue contained only carbonate and the meta salt and the latter had appropriated 2 molecules of water, the calculated weight of the mixture would have been 0.44027 gram instead of 0.44427 gram, as it was found to be. The difference of only 4 mgms. between the two weights suggests the possibility that the excess of weight was not due to the decomposition of the metaborate by the gas, but to the presence of water in the former. It will be shown by a later experiment that when carbon dioxide, either dry or saturated with water vapor, is passed over dry metaborate of barium, the gas is not

absorbed at any temperature between that of the air and a red heat. This fact, however, proves nothing as to what may occur when the salt is more or less in the dissolved condition.

The fact that no increase in weight was observed when (2) the residue, after the first drying, was again moistened and exposed for forty-eight hours in an atmosphere of carbon dioxide, appears to show that the gas had produced its maximum effect, under the conditions, during the first evaporation. Nevertheless, the action of the carbon dioxide could not have proceeded so far as to convert all of the barium into carbonate; for, if the residue had consisted of $BaCO_3 + H_3BO_3$, the weight would have been 0.52733 gram; if of $BaCO_3 + HBO_2$, it would have been 0.47677 gram; while, if the mixture had consisted of $BaCO_3 + B_2O_3$, we should have had a weight of 0.45149 gram. The last supposition is, of course, inadmissible in view of the low temperature to which the residue was heated. Since all of these weights are higher than that obtained, the obvious conclusion is that our mixture, when first weighed, could not have consisted of carbonate and free boric acid, but rather that it consisted either of carbonate and metaborate containing water, or of carbonate and a more acid borate than the meta salt. The only alternative explanation of the excess of weight involves a considerable loss of boric acid by volatilization.

Experiment XIV. was duplicated except that the residue, after the first evaporation, was moistened with water and again dried on the bath in an atmosphere of carbon dioxide, and then heated for ten minutes over a single burner before weighing. The results were similar to those of XIV. The first weight was too large by 0.0156 gram, but, after five successive ignitions over a triple burner, it was too small by 0.0207 gram for a mixture of carbonate and metaborate. These losses at high temperatures are ascribed without much hesitation to the expulsion of carbon dioxide, since it is proved by a later experiment that the gas is liberated under analogous conditions.

In order to determine beyond question the composition of the residues and the nature of the overweight which is observed under conditions similar to those already described, it

will be necessary to supplement experiments like XIV. and XV., and others to be described hereafter, by still others in which the volatile products are collected from stage to stage and weighed. We had expected to do this, and shall utilize the first opportunity to carry out our plan.

Experiment XVI.

Weight BaO = 0.3144 gram = 0.40457 gram $BaCO_3$.

" B_2O_3 = 0.08019 gram = 0.14203 gram H_3BO_3 = 0.1008 gram HBO_2 = 0.25546 gram $BaO.B_2O_3$.

Excess of BaO = 0.13838 gram = 0.25611 gram $BaCO_3$.

Weight of mixture, if consisting of $BaO.B_2O_3$ and $BaCO_3$ only, = 0.43428 gram.

Volume of mixed solutions (31.87 cc. $Ba(OH)_2$ and 11.46 cc. H_3BO_3) = 43.33 cc.

The vessel containing the mixed liquids was placed under a bell-jar which was connected at the top with a carbon dioxide generator, and allowed to stand for an hour. It was then placed on a water-bath, the liquid evaporated, and the apparently dry residue heated for four hours. Carbon dioxide was not passed into the dish during the evaporation.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $BaO.B_2O_3$ + $BaCO_3$. Gram.
1. First weighing	0.54003	.....	+0.10575
2. Stood 1¾ hours in the air	0.54140	+0.00137	+0.10712
3. Heated ½ hour on water-bath	0.53919	—0.00221	+0.10491
4. Stood 14½ hours in the air	0.53998	+0.00079	+0.10630
5. Heated ¼ hour on water-bath	0.53811	—0.00187	+0.10383
6. Stood 1 hour in the air	0.53958	+0.00147	+0.10530
7. " 6 days "	0.54078	+0.00120	+0.10650
8. Heated 3½ hours at 100° in air-bath	0.53821	—0.00257	+0.10393
9. Stood 7¾ hours in the air	0.53921	+0.00100	+0.10493
10. Heated 3½ hours at 100° in air-bath	0.53510	—0.00411	+0.10082
11. Stood 25½ hours in the air	0.53815	+0.00305	+0.10387
12. Heated 1 hour at 100° in air-bath	0.53370	—0.00445	+0.09942
13. Stood 4 hours in the air	0.53719	+0.00349	+0.10291
14. Heated 1 hour at 110°	0.53253	—0.00466	+0.09825

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $BaO.B_2O_3 + BaCO_3$. Gram.
15. Stood 4 hours in the air	0.53554	+0.00301	+0.10126
16. Heated 1 hour at 110°	0.53109	—0.00445	+0.09681
17. Stood 1½ hours in the air	0.53423	+0.00314	+0.09995
18. Heated 2 hours at 110°	0.53173	—0.00250	+0.09745
19. Stood 3¾ hours in the air	0.53403	+0.00230	+0.09975
20. Heated 4¼ hours at 110°	0.53380	—0.00023	+0.09952
21. Stood 1½ hours in the air	0.53462	+0.00082	+0.10034

In the preceding table the material is stated to have stood for various periods of time in the air, and the weights given are those found at the close of these periods; in every case, however, several intermediate weighings were made and the exposure was not discontinued until the increase in weight in the air became insignificant.

The results are believed to have some bearing on the question of the actual liberation of boric acid in consequence of the action of carbon dioxide on the mixture. If all of the barium had been converted into carbonate, and all of the boric acid had been liberated as H_3BO_3, the combined weight of the two would have been 0.5466 gram, which is only 0.0066 gram greater than the first weight found after the last heating upon the water-bath (No. 5). This fact might be construed, at first sight, as evidence of such a reaction, but the subsequent conduct of the material when heated in the air-bath shows that free boric acid (H_3BO_3) could not have been present; for, after heating three and one-half hours at 100° (No. 8), the change in weight from the last heating upon the water-bath (No. 5) was —0.0001 gram, which, of course, has no significance whatever. On subsequently heating to the same temperature for four and one-sixth hours in all (Nos. 10 and 12), the loss amounted to 0.00451 gram; but on standing in the air for four hours (No. 13), all of this, except 1 mgm., was recovered. Again, on heating to the higher temperature of 110° (Nos. 14, 16, 18, and 20) for various periods, amounting altogether to eight and a quarter hours, the loss from the last heating at 100° amounted only to 0.0044 gram; and after each heating (except the final one when the exposure was only one

and a half hours), the material showed a tendency to recover in the air what it had lost in the bath. These slight losses and their subsequent recovery in the air indicate the presence of a salt containing water, and disprove, we think, the presence of any weighable quantity of the free acid; since boric acid, H_3BO_3, is said to lose water at 100° and to pass at that temperature into the meta acid, HBO_2. It is perhaps useless to speculate seriously as to what hydrated salt was present, but it is to be noted that either $BaOB_2O_3.5H_2O$, or $BaO(B_2O_3)_2.7H_2O$—the superfluous barium being in the form of carbonate—would have given weights very nearly equal to those which were obtained. The first would have given the weight 0.53184 gram, and the second the weight 0.53193 gram, while the weight obtained after the last heating to 110° was 0.5338 gram. These coincidences, however, we do not regard as having any particular weight since, doubtless, still other possible hydrated acid salts would satisfy the conditions equally well.

Experiment XVII.

Weight BaO = 0.51673 gram = 0.66492 gram $BaCO_3$.
" B_2O_3 = 0.09871 gram B_2O_3 = 0.17484 gram H_3BO_3.
= 0.12409 gram HBO_2 = 0.31446 gram $BaO.B_2O_3$.
Excess of BaO = 0.30006 gram = 0.38703 gram $BaCO_3$.
Weight of mixture, if consisting of $BaO.B_2O_3$ and $BaCO_3$ only, = 0.70149 gram.
Volume of mixed solutions (36.00 cc. Ba(OH)$_2$ and 14.13 cc. H_3BO_3) = 50.13 cc.

The liquid was evaporated to a small volume on the water-bath, and then treated for one-half hour with carbon dioxide without removal from the bath. The current was discontinued and the residue evaporated to dryness.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $BaO.B_2O_3 + BaCO_3$. Gram.
1. First weighing	0.72571	.....	+0.02422
2. Stood 1½ hours in the air	0.72652	+0.00081	+0.02503
3. Heated 3½ hours at 100° in air-bath	0.72291	−0.00361	+0.02142
4. Stood 7½ hours in air (7 intermediate weighings)	0.72581	+0.00290	+0.02432
5. Heated 3½ hours at 100° in air-bath	0.72300	−0.00281	+0.02151
6. Stood 5½ hours in the air (6 intermediate weighings)	0.72412	+0.00112	+0.02263
7. Heated 1 hour at 100° in air-bath	0.72175	−0.00237	+0.02026
8. Stood 4½ hours in the air (5 intermediate weighings)	0.72275	+0.00100	+0.02126
9. Heated 1 hour at 110°	0.71984	−0.00291	+0.01835
10. Stood 4 hours in the air (5 intermediate weighings)	0.72147	+0.00163	+0.01998
11. Heated 1 hour at 110°	0.71886	−0.00261	+0.01737
12. Stood 1½ hours in the air (3 intermediate weighings)	0.72183	+0.00297	+0.02034
13. Heated 2 hours at 110°	0.71750	−0.00433	+0.01601
14. Stood 3¾ hours in the air (5 intermediate weighings)	0.72172	+0.00422	+0.02023

The material exhibited very much the same conduct in this as in the preceding experiment. When heated for seven and two-thirds hours at 100°, it lost in the former case from the first weighing 0.00633 gram and regained in the air 0.00349 gram, the net loss at 100°, with subsequent exposure, being 0.00294 gram; while in the latter case, with a heating of eight hours, with subsequent exposure, the net loss was 0.00296 gram. The net changes in weight at 110°, from the last weights at 100°, were, in the former instance, +0.0007 gram, and in the latter, −0.00003 gram. The inference might perhaps be drawn from this similarity of conduct that the same salt was formed in both instances, notwithstanding the different manner in which the two mixtures were treated with carbon dioxide. If all of the boric acid were present in the residue in Experiment XVII. as $BaOB_2O_4H_2O$, the weight should have been 0.72693 gram, which differs only 0.00172 gram from

the first weight obtained after removing the dish from the water-bath. However, the supposition that a metaborate containing only 1 molecule of water was formed would by no means account for all the weight obtained in Experiment XVI. It is therefore concluded that either different acid salts were formed, or, if the same salt was produced, it differed in the two cases in its degree of hydration.

Experiment XVIII.

Weight BaO = 0.68545 gram = 0.88203 gram $BaCO_3$.
" B_2O_3 = 0.10148 gram = 0.18013 gram H_3BO_3.
= 0.12756 gram HBO_2 = 0.32423 gram $BaOB_2O_3$.
Excess of BaO = 0.46271 gram = 0.59551 gram $BaCO_3$.
Weight of mixture, if consisting of $BaOB_2O_3$ and $BaCO_3$ only, = 0.91963 gram.
Volume of mixed solutions (31.26 cc. Ba(OH)$_2$ and 14.45 cc. H_3BO_3) = 45.71 cc.

Carbon dioxide was passed over the material during the entire time of the evaporation upon the water-bath, and the residue was heated to 120° for two and a half hours before weighing.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $BaOB_2O_3$ + $BaCO_3$. Gram.
1. First weighing	0.94014	.....	+0.02051
2. Heated 3¾ hours at 120° (3 intermediate weighings)	0.93961	−0.00053	+0.01998
3. Heated 12⅛ hours at 110° (2 intermediate weighings)	0.94395	+0.00434	+0.02432
4. Heated 60⅛ hours at 150° (11 intermediate weighings)	0.93057	−0.01238	+0.01094
5. Heated 9 hours at 175°	0.92560	−0.00497	+0.00597
6. Heated 23 hours at 175°	0.92109	−0.00451	+0.00146
7. Heated 3½ hours at 175°	0.92296	+0.00187	+0.00333
8. Heated 9½ hours at 175°	0.92305	+0.00009	+0.00342

Experiment XIX.

Weight BaO = 0.68685 gram = 0.88383 gram $BaCO_3$.
" B_2O_3 = 0.10106 gram = 0.17938 gram H_3BO_3 = 0.12703 gram HBO_2 = 0.32252 gram $BaOB_2O_3$.
Excess of BaO = 0.46503 gram = 0.59849 gram $BaCO_3$.

Weight of mixture, if consisting of $BaOB_2O_3$ and $BaCO_3$ only, = 0.92127 gram.

Volume of mixed solutions (31.41 cc. $Ba(OH)_2$ and 14.39 cc. H_3BO_3) = 45.80 cc.

The treatment with carbon dioxide was the same as in XVIII.; that is, the gas was passed over the material during the entire time occupied in the evaporation upon the water-bath. The residue, as in the case of No. XVIII., was heated to 120° for two and a half hours before weighing.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $BaO.B_2O_3 + BaCO_3$. Gram.
1. First weighing	0.93846	.....	+0.01719
2. Heated 1¾ hours at 120°	0.93230	—0.00616	+0.01103
3. Heated 2 hours at 120° (2 weighings)	0.93306	+0.00076	+0.01179
4. Heated 12½ hours at 110° (2 weighings)	0.93501	+0.00195	+0.01374
5. Heated 88¾ hours at 150° (11 weighings)	0.92515	—0.00986	+0.00388
6. Heated 44 hours at 175° (4 weighings)	0.91964	—0.00551	—0.00163

Nos. XVIII. and XIX. are duplicates. Both residues exhibit a tendency to lose weight slowly when the temperature is raised from 120° to 150° and 175°, and to gain weight when the temperature is lowered from 120° to 110°. At 175° both approach the theoretical weight for a mixture of $BaOB_2O_3$ and $BaCO_3$. The calculated weight for a mixture of $BaOB_2O_3H_2O$ and $BaCO_3$ was, for No. XVIII., 0.94578 gram, for No. XIX., 0.94732 gram; while the first weights found were 0.94014 gram and 0.93846 gram, respectively. The differences are 0.00564 gram and 0.00718 gram.

Experiment XX.

Weight BaO = 0.56113 gram = 0.72217 gram $BaCO_3$.

" B_2O_3 = 0.12592 gram = 0.27638 gram BaO, if $BaOB_2O_3$ is formed, = 0.40230 gram $BaOB_2O_3$.

Excess of BaO = 0.28475 gram = 0.3664 gram $BaCO_3$.

Weight of mixture, if consisting of $BaOB_2O_3$ and $BaCO_3$ only, = 0.7687 gram.

Volume of mixed solutions (20.39 cc. $Ba(OH)_2$ and 16.90 cc. B_2O_3) = 37.29 cc.

The liquid was evaporated to a small volume on the water-bath and then treated, still hot, for fifteen minutes with carbon dioxide. During the latter period the contents of the dish were stirred with a platinum rod. The drying of the residue was completed on an iron plate.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $BaOB_2O_3 + BaCO_3$. Gram.
1. Heated to redness over burner	0.75126	.....	—0.01744
2. " " " " "	0.74996	—0.0013	—0.01874
3. Stood in the air 18 hours (2 weighings)	0.76632	+0.01636	—0.00238
4. Stood in the air 48 hours	0.77439	+0.00807	+0.00569
5. " " " " 50½ "	0.77410	—0.00029	+0.00540
6. Heated to redness o'er burner	0.75361	—0.02049	—0.01509
7. " " " " "	0.75605	+0.00244	—0.01265
8. " " " " "	0.75418	—0.00187	—0.01452
9. Moistened with water, saturated with CO_2, and heated cautiously over burner	0.76669	+0.01251	—0.00201
10. Repeated treatment No. 9	0.77036	+0.00367	+0.00166

The results obtained in No. XX. show that when carbon dioxide has been lost in consequence of excessive heating, and the material is exposed to the air, there is a recovery of weight (Nos. 3 and 4), which must, of course, be due to the absorption of water or carbon dioxide, or of both. The increase in weight ceases after a time (No. 5), but the stable weight reached in this manner somewhat exceeds that calculated for a mixture of $BaOB_2O_3 + BaCO_3$. When the residue is moistened with water, treated with carbon dioxide, and afterwards heated more cautiously, as in Nos. 9 and 10, its weight again approaches that estimated for a mixture of metaborate and carbonate.

Experiment XXI.

Weight BaO = 0.29846 gram = 0.38406 gram $BaCO_3$.

" B_2O_3 = 0.06682 gram = 0.14777 gram BaO, if $BaO.B_2O_3$ is formed = 0.21488 gram $BaO.B_2O_3$.

Excess of BaO = 0.15069 gram = 0.19394 gram $BaCO_3$.

Weight of mixture, if consisting of $BaOB_2O_3$ and $BaCO_3$ only, = 0.40882 gram.

Volume of mixed solutions (10.85 cc. $Ba(OH)_2$ and 8.97 cc. H_3BO_3) = 19.82 cc.

The liquid was evaporated to a small volume on the water-bath and then treated for fifteen minutes with carbon dioxide (as in XX.). The dried residue was heated to redness and weighed.

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $BaO.B_2O_3 + BaCO_3$. Gram.
1. First weighing	0.40294	.....	−0.00588
2. Heated to redness	0.40076	−0.00218	−0.00806
3. Stood in air 20 hours (2 weighings	0.40817	+0.00741	−0.00065
4. Stood in air 65 hours	0.41108	+0.00291	+0.00226
5. " " " 67½ "	0.41198	+0.00090	+0.00316
6. " " " 71½ "	0.41088	−0.00110	+0.00206
7. Moistened with water, treated with CO_2, using phenolphthalein, and heated to redness	0.41952	+0.00864	+0.01070
8. Heated to redness	0.41563	−0.00389	+0.00681
9. " " "	0.41187	−0.00376	+0.00305
10. " " "	0.41040	−0.00147	+0.00158
11. " " "	0.40939	−0.00101	+0.00057
12. Repeated treatment No. 7	0.41783	+0.00844	+0.00901
13. " " Nos. 7 and 12	0.41280	−0.00503	+0.00398
14. Heated to redness	0.41012	−0.00268	+0.00130
15. Heated longer and higher than in No. 14	0.40366	−0.00646	−0.00516
16. Heated to redness	0.40198	−0.00168	−0.00684
17. " " "	0.40164	−0.00034	−0.00718
18. Stood 2½ hours in air (6 weighings)	0.40623	+0.00459	−0.00259
19. Stood 2½ hours in air (2 weighings)	0.40751	+0.00128	−0.00131
20. Stood 1⅝ hours in the air	0.40800	+0.00049	−0.00082
21. " 3 " " " "	0.40899	+0.00099	−0.00017
22. " 24 " " " "	0.41037	+0.00138	+0.00155
23. Stood over $CaCl_2$ 2 hours	0.40983	−0.00054	+0.00101
24. " " " 7 "	0.40969	−0.00014	+0.00087
25. " " " 9 "	0.40947	−0.00022	+0.00065
26. " " " 24 "	0.40941	−0.00006	+0.00059

	Weight of residue. Gram.	Change of weight. Gram.	Variation from wt. of $BaO.B_2O_3 + BaCO_3$. Gram.
27. Heated to redness	0.40495	—0.00446	—0.00387
28. " " "	0.40352	—0.00143	—0.00530
29. " " "	0.39733	—0.00619	—0.01149
30. " " "	0.39746	+0.00013	—0.01136
31. " " "	0.39709	—0.00037	—0.01173
32. " " "	0.39722	+0.00013	—0.01160
33. " " "	0.39732	+0.00010	—0.01150
34. " " "	0.39624	—0.00108	—0.01258
35. Repeated treatment Nos. 7, 12, and 13	0.41112	+0.01488	+0.00230
36. Repeated treatment Nos. 27 to 33 (7 weighings)	0.39948	—0.01164	—0.00934
37. Stood 15 hours in the air	0.40898	+0.0095	+0.00016
38. " 37 " " " " " (2 weighings)	0.40931	+0.00033	+0.00049
39. Stood 22 hours in the air	0.40959	+0.00028	+0.00077
40. " 39 " " " "	0.41045	+0.00086	+0.00163
41. " over $CaCl_2$ 3 hours	0.40939	—0.00106	+0.00057
42. " " " $6\frac{1}{2}$ "	0.40948	+0.00009	+0.00066

Our experiments XXII. to XXVI. inclusive, were similar to XXI., except that the manner of treating the mixed liquids with carbon dioxide was varied to some extent. In most of them phenolphthalein was added to the liquid and the treatment with the gas discontinued when the color disappeared. The results only confirm the obvious conclusions to be drawn from the data already presented, and we therefore omit them. These conclusions are :

1. At a full red heat the meta salt attacks the carbonate with expulsion of carbon dioxide.

2. The temperature at which a mixture of the metaborate and the carbonate of barium is stable and which is still sufficiently high to insure the dehydration of the former appears to be just under a red heat.

3. If a mixture of the metaborate and carbonate has been heated too high, *i. e.* so high that some of the latter has been decomposed with formation presumably of a more basic borate, the lost weight is restored by exposing the material to the air. The weight gained through the exposure is slightly greater than is required to bring the mixture up to the theo-

retical weight, but the excess is lost when the mixture is placed in a desiccator. The experiment of heating the material, after treatment with carbon dioxide, until the weight fell below that calculated for a mixture of metaborate and carbonate, and then of exposing it in the air until the weight became very nearly constant, and, finally, of removing the slight excess of weight by placing the material over calcium chloride or sulphuric acid, was many times repeated and always with a satisfactory degree of success except in two cases. In these it was suspected that, while some portions of the material had been heated high enough to decompose the carbonate, other portions had not reached the temperature required for the complete dehydration of the metaborate; for it was observed that the weights gained in the air on these occasions far exceeded the calculated deficits.

4. If the material which has been reduced below its theoretical weight by prolonged ignition is moistened with water and then treated with carbon dioxide, it quickly gains not only the weight required for a mixture of metaborate and carbonate, but considerable besides. Whether the excess of weight so acquired is due to the formation of more acid borates or to the acquisition of water by the meta salt, or to both causes, can be ascertained only by collecting and determining the compounds which are volatilized when the product is again heated.

In Experiments XXVII. to XXX., inclusive, an iron bath surrounded by asbestos board and a mercury thermometer for high temperatures were employed. By placing three burners under the bath, the temperature could be raised at times somewhat beyond the range of the thermometer, *i. e.*, above 550°; at other times, however, with the same arrangement of lamps, the temperature would not rise above 460° or 470°.

Experiment XXVII.

Weight BaO = 0.38103 gram = 0.49030 gram $BaCO_3$.
" B_2O_3 = 0.09200 gram = 0.20194 gram BaO, if converted into $BaOB_2O_3$ = 0.29394 gram $BaOB_2O_3$.
Excess BaO = 0.17909 gram = 0.23045 gram $BaCO_3$.

Weight of mixture, if consisting of $BaOB_2O_3$ and $BaCO_3$ only, = 0.52439 gram.

Volume of mixed solutions (14.93 cc. $Ba(OH)_2$ and 12.37 cc. H_3BO_3) = 27.2 cc.

The mixed solutions were treated with phenolphthalein and then, cold, with carbon dioxide for five minutes after the color had disappeared. After evaporation to dryness on the water-bath, the residue was heated in the air-bath previously mentioned.

	Weight of residue. Gram.	Change in weight. Gram.	Variation from wt. of $BaOB_2O_3$ + $BaCO_3$. Gram.
1. Heated 5 hours at 450°–470°	0.55756	.....	+0.03317
2. Stood 1½ hours in the air	0.56011	+0.00255	+0.03572
3. Heated 11¼ hours over 3 burners (3 weighings)	0.54682	—0.01329	+0.02243
4. Heated 9 hours over 3 burners	0.53219	—0.01463	+0.00780
5. Heated 6 hours over 3 burners	0.52244	—0.00975	—0.00195
6. Stood 3 hours in the air	0.52703	+0.00460	+0.00265
7. Stood 24 hours in the air	0.52817	+0.0011	+0.00378
8. Stood 48 hours over H_2SO_4	0.52761	—0.00056	+0.00322
9. Heated 7 hours over 3 burners	0.52177	—0.00584	—0.00262
10. Stood 4¾ hours in the air	0.52586	+0.00409	+0.00147
11. " 8 hours in the air	0.52637	+0.00051	+0.00198
12. " 24 hours in the air	0.52685	+0.00048	+0.00246
13. " 36 " over H_2SO_4 (3 weighings)	0.52638	—0.00047	+0.00199
14. Heated 9 hours at 450°–475°	0.52497	—0.00141	+0.00058
15. Stood 24 hours in the air	0.5261	+0.00113	+0.00171
16 " 48 " over H_2SO_4	0.52597	—0.00013	+0.00158
17. Heated out of bath to redness	0.51584	—0.01013	—0.00855
18. Stood 6 hours over dilute solution of KOH	0.53680	+0.02096	+0.01241
19. Stood 66½ hours over H_2SO_4	0.52577	—0.01103	+0.00138
20. " 68½ " " "	0.52574	—0.00003	+0.00135
21. Heated 7 hours at 450°–470°	0.52359	—0.00215	—0.00080
22. Stood in air 1 hour	0.52405	+0.00046	—0.00034
23. Heated 4 hours at 460°–470°	0.52480	+0.00075	+0.00041
24. Stood 1 hour in air	0.52485	+0.00005	+0.00046
25. Heated 9 hours in bath over 3 burners	0.52733	+0.00248	+0.00294
26. Stood ¼ hour in air	0.52754	+0.00021	+0.00315
27. Heated out of bath over burner	0.52180	—0.00574	—0.00259

		Weight of residue. Gram.	Change in weight. Gram.	Variation from wt. of $BaOB_2O_3$ + $BaCO_3$. Gram.
28.	Heated 2 hours at 450°–470°	0.52517	+0.00337	+0.00078
29.	" 1 hour " 450°–470°	0.52537	+0.00020	+0.00098
30.	" " " " 450°–470°	0.52554	+0.00017	+0.00115
31.	" out of bath over burner	0.51902	—0.00652	—0.00537
32.	Heated 1 hour at 450°–460°	0.52225	+0.00323	—0.00214
33.	" " " " 440°–460°	0.52365	+0.00140	—0.00074
34.	" " " in bath over 3 burners and allowed to cool in the bath	0.52431	+0.00066	—0.00008
35.	Repeated No. 34	0.52446	+0.00015	+0.00007
36.	" " "	0.52459	+0.00013	+0.00020
37.	" " "	0.52480	+0.00021	+0.00041
38.	" " "	0.52496	+0.00016	+0.00057
39.	" " "	0.52511	+0.00015	+0.00072

Experiments XXVIII., XXIX., and XXX. resembled XXVII. very closely, and the results were so similar to those recorded under that number that they need not be given here in detail. In general, it was found difficult, by heating in our bath, to bring the too great initial weight of the material down to that calculated for a mixture of metaborate and carbonate, though in one case (No. XXX.) this was accomplished by heating in the bath for three hours over three burners. The temperature on this occasion, however, rose so high that the thermometer was removed. The conduct of the material in the air, after having been heated, appeared to be contradictory. At times the weight would rise in the air from slightly below the theoretical to several milligrams above it, and only a part of the excess would disappear over sulphuric acid; while at other times, the gain in the air would carry the weight only slightly above the theoretical, and then the loss in the desiccator would just about suffice to reduce it to that calculated for a mixture of metaborate and carbonate. We have only a provisional explanation to offer for this conduct. It was noticed in some of the earlier experiments, in which the material had been much more highly heated and the weight greatly reduced thereby, that, on exposure to the air, it gained only enough to carry its weight a little above the normal, and

that nearly all of the excess was lost in the desiccator. And on comparing the later experiments with the earlier, it was found that the same thing occurred in those instances in which the weight of the material had previously been reduced several milligrams below the theoretical weight. This led us to suspect that the temperature at which complete dehydration occurs and that at which the metaborate begins to attack the carbonate do not lie very far apart, and that a salt which has not been completely dehydrated is capable of taking on more water from the air, while one which has been heated high enough to expel all of the water is comparatively indifferent to atmospheric moisture. In these later experiments, as in the earlier ones, there was no difficulty in obtaining nearly theoretical results by heating the material until its weight was considerably below that calculated for a mixture of carbonate and metaborate, then exposing it to the air until the weight became nearly constant, and finally drying in a desiccator, or heating to a temperature approaching 500°. From this it appears probable that the more basic borate which is formed at high temperatures is decomposed at ordinary temperatures by the carbon dioxide of the air and reconverted into the metaborate and carbonate. A similar absorption of carbon dioxide takes place when material whose weight has been reduced below the normal amount is reheated in the bath at temperatures under 500°. From this it is inferred that normal weights could be quickly obtained by first heating to a high temperature and then at a lower one, but we have not yet tried the experiment.

A notable increase in weight over a dilute solution of potassium hydroxide is recorded (XXVII., 18). In another similar case, material weighing 0.51882 gram gained in the same way 26 mgms. and subsequently lost 13 mgms. over sulphuric acid. Placed over the alkali again, it gained 23 mgms. and afterwards lost 17 mgms. in the desiccator. In a third instance, on the other hand, material (0.25729 gram) which had been brought within 0.0008 gram of normal weight, gained only 1.6 mgms. over a solution of potassium hydroxide, and more than half of this increase was lost over sulphuric acid. The increase in weight over potassium hydroxide could have

been due only to the absorption of water, and the difference in conduct is perhaps to be explained in the same way as the contradictory behavior of different specimens of material in the air.

At the time our work was interrupted we were engaged in an endeavor to ascertain how a mixture of known quantities of barium metaborate and carbonate conducts itself when heated to different temperatures, both in the absence and in the presence of carbon dioxide. To prepare the metaborate, equal volumes of equivalent solutions of boric acid and barium hydroxide were mixed, the former being poured into the latter. A precipitate formed, which was dissolved by passing steam into the liquid. A slight cloudiness—supposed to be due to barium carbonate—remained. The solution was filtered, and to portions of the filtrate equal volumes of 95 per cent alcohol were added. The mixture was allowed to stand for three days undisturbed, though at the end of twenty-four hours the precipitate exhibited a distinctly crystalline appearance. After filtering, the material was washed with alcohol, air-dried upon unglazed porcelain plates, and analyzed. It proved to be the metaborate with 5 molecules of water. From a portion of the filtrate, which was not treated with alcohol, wart-like and very compact bunches of crystals separated within a few days, which were found to have the same composition as the material obtained from the alcoholic liquid. Specimens from the two sources gave 28.97 and 28.89 per cent of water, respectively, while the percentage of water in $BaOB_2O_4.5H_2O$ is 28.74. Some of the dehydrated salt which was used in the subsequent experiments gave 68.05 per cent of BaO against 68.7 per cent calculated for $BaOB_2O_3$.

Experiment XXXI.

0.97778 gram of the hydrated metaborate, in a platinum boat, was placed in a combustion tube and heated to constant weight in a current of dry air, which had been deprived of its carbon dioxide. The loss in weight was 0.028418 gram = 28.06 per cent. The dehydrated material was next heated in a current, first of dry and then of moist carbon dioxide.

	Weight of material. Gram.	Change in weight. Gram.
1. 2 hours at full red heat in dry CO_2	0.69454	+0.00094
2. " " as in 1	0.69485	+0.00031
3. 2 hours at lower temperature than in 1 and 2	0.69508	+0.00023
4. 1½ " " " " " " 3	0.69500	—0.00008
5. 1 " " " " " " 4	0.69472	—0.00028
6. 2 " " " " in CO_2 saturated with water vapor	0.69540	+0.00068
7. 2 hours as in 6, but at higher temperature	0.69483	—0.00057
8. 2 " at full red heat, CO_2 saturated with water vapor as in 6 and 7	0.69371	—0.00112
9. 2 hours at red heat as in 8	0.69369	—0.00002
10. Stood in the air 28¾ hours (5 weighings)	0.69436	+0.00067

The results recorded above indicate that the metaborate of barium is incapable of absorbing carbon dioxide when exposed, at high or low temperatures, in a dry or in a moist atmosphere of that gas; also, that when the salt has been once fully dehydrated, it does not take on an appreciable amount of water in the air. But, as remarked elsewhere, the salt may well conduct itself differently towards carbon dioxide when it is dissolved or suspended in water, as it apparently does towards atmospheric moisture when partially hydrated.

Barium carbonate was next prepared, and the constancy of its weight at high temperature, both in dry and moist carbon dioxide, demonstrated. It was mixed with an equivalent quantity of dehydrated metaborate, and a weighed amount of the mixture was heated in a combustion tube under the conditions specified below. The experiment was a preliminary one and the statements regarding temperature are, of course, very indefinite.

Experiment XXXII.

Weight of mixture of $BaOB_2O_3$ + $BaCO_3$ = 1.28219 gram.

	Weight of material. Grams.	Change in weight. Grams.	Variation from original weight. Grams.
1. Heated gently 2 hours in a current of air free from CO_2	1.28214	—0.00005	—0.00005
2. Heated 2½ hours in a current of air to a temperature at which the glass softened	1.19321	—0.08893	—0.08898

	Weight of material. Grams.	Change in weight. Grams.	Variation from original weight. Grams.
3. Heated 2 hours as in 2	1.19232	—0.00089	—0.08987
4. Heated at a somewhat lower temperature in current of dry CO_2	1.19325	+0.00093	—0.08894
5. Stood 1 hour at temperature of room in dry CO_2	1.19343	+0.00018	—0.08876
6. Warmed the material 1 hour in current of dry CO_2	1.19869	+0.00526	—0.08350
7. Warmed 1 hour as in 6	1.19965	+0.00096	—0.08254
8. Heated 1 hour, higher than in 6 and 7, but still in dry current of CO_2	1.21168	+0.01203	—0.07041
9. Heated 51 hours as in 8 (16 weighings)	1.28097	+0.06929	—0.00122
10. Heated 8 hours as in 8 and 9	1.28134	+0.00037	—0.00085
11. " 35 " to a higher temperature, but still under a red heat, current of CO_2 continued (7 weighings)	1.28333	+0.00199	+0.00114
12. Heated 7 hours to redness in current of dry CO_2	1.23357	—0.04976	—0.04862
13. Heated 39 hours as in 12 (5 weighings)	1.18647	—0.04710	—0.09572
14. Heated 8 hours to redness in moist CO_2	1.21508	+0.02861	—0.06711
15. Heated 8 hours as in 14	1.21552	+0.00044	—0.06711
16. " 8 " to redness in air free from CO_2 and H_2O	1.18599	—0.02953	—0.09620
17. Heated 8 hours to redness in current of moist CO_2	1.18658	+0.00059	—0.09561
18. Heated 78 hours at varying low temperatures in current of moist CO_2	1.26457	+0.07799	—0.01762

The experimental work which we have here described is to be regarded as preliminary only. It was undertaken for the purpose of securing sufficient data to enable us to attack advantageously the problem we had in mind. If we had been able to complete our investigation without interruption, or if the circumstances under which it was commenced had been different, doubtless much that we have recorded, having been found unessential, would have been suppressed. The work will be resumed at the earliest opportunity.

THE COMPOSITION OF NITROGEN IODIDE.

By F. D. Chattaway.

Black explosive compounds formed by the interaction of iodine, or compounds containing iodine, with ammonia have been analyzed from time to time during the past century, but in very few cases do the results agree, those of the same observer, even, often differing widely. It is usually stated that a number of distinct compounds exist, but the statement is based entirely on these discordant results.

Upon close examination most of the analyses prove untrustworthy, for in no case is any evidence brought forward to show that the material analyzed was pure, and in no case are any data given to justify the assumptions made regarding the reactions on which the analyses are based.

Such black explosive substances, both crystalline and amorphous, but resembling each other closely in properties, having been prepared in many ways in a state of undoubted purity, this investigation was undertaken to determine their composition, and to find out whether more than one definite compound could be produced.

Nitrogen iodide so frequently decomposes in more than one way under the influence of reagents that it was a matter of difficulty to find a suitable reaction to employ in its analysis, and to determine the conditions necessary for known products to be formed which admitted of quick and easy estimation. Such a reaction was found, however, in the decomposition of nitrogen iodide by sodium sulphite. In this, if light be excluded, all the nitrogen is obtained as ammonia and all the iodine as hydriodic acid. These can easily be estimated, and the relation between the nitrogen and iodine in any specimen of nitrogen iodide obtained.

This relation is found to be absolutely invariable, 2 molecules of ammonia are always produced to every 3 molecules of hydriodic acid. However the nitrogen iodide is prepared, and whatever its condition, dry or moist, crystalline or amorphous, compact or finely divided, it is the same. This proves that in all reactions which are known to yield nitrogen

iodide only one compound is formed, and that in its molecule 2 atoms of nitrogen are associated with 3 atoms of iodine.

Now, when nitrogen iodide decomposes under the influence of light it breaks up quantitatively into nitrogen and hydriodic acid.[1] Consequently its molecule must contain the same number of atoms of hydrogen as it does atoms of iodine. Since, therefore, in its molecule 2 atoms of nitrogen are associated with 3 atoms of iodine, and these again with 3 atoms of hydrogen, the simplest possible formula for nitrogen iodide is $N_2H_3I_3$.

That this formula does represent the composition of nitrogen iodide has been further proved by a large number of analyses of weighed amounts of the pure dry substance prepared in different ways. The percentages of nitrogen and of iodine found agree accurately with those required by this formula.

Further, all attempts to prepare similar bodies of a different composition have completely failed.

It may be taken, therefore, as a definitely proved fact that only one substance of the nature of nitrogen iodide has hitherto been prepared, and that the composition of this is represented by the formula $N_2H_3I_3$. The weight of the molecule and the exact manner in which the atoms are linked together still remain to be settled.

EXPERIMENTAL PART.

Investigation of the Reaction Employed for Determining the Composition of Nitrogen Iodide.

When sodium sulphite is slowly added to nitrogen iodide suspended in water until the latter is completely decomposed and the brown color of the liberated iodine just disappears, a colorless acid solution is obtained containing only sodium sulphate, ammonium iodide, and free hydriodic acid. This reaction, one of a very few where nitrogen iodide decomposes in one way only, has been thoroughly investigated in order to base upon it a method of analysis.

The sulphate produced was first shown to be exactly equivalent to the sulphite used. An unknown quantity of nitrogen iodide was titrated with decinormal sodium sulphite and the

[1] See "Action of Light on Nitrogen Iodide", page 159.

resulting sulphate estimated by precipitation with barium chloride.

Two experiments were made: in one 59.3 cc. of decinormal sodium sulphite were used and 0.6914 gram of barium sulphate obtained; in the other 62.5 cc. were used and 0.7288 gram obtained, the weights of barium sulphate equivalent to the quantities of sulphite used being 0.6908 gram and 0.7281 gram, respectively.

The fact was next established that ammonia is the sole compound formed that contains nitrogen. Careful examination showed that neither nitrite, nitrate, hydroxylamine, nor hydrazine was produced.

On distilling with potash, the product obtained by decomposing a large quantity of nitrogen iodide by sodium sulphite an alkaline gas was evolved. This was absorbed by hydrochloric acid and the solution evaporated to dryness. The salt so formed proved to be pure ammonium chloride. On distillation with alkali it gave the theoretical quantity of ammonia, and with platinum chloride it formed ammonium platinic chloride yielding the theoretical weight of platinum on heating.

In two estimations with different specimens of the salt 1.2341 grams and 1.5273 grams yielded 23.1 cc. and 28.5 cc. of decinormal ammonia, theory requiring from ammonium chloride 23.06 cc. and 28.54 cc., respectively.

In three estimations with specimens prepared at different times, 1.8994 grams, 0.7098 gram, 0.8912 gram yielded 0.8361 gram, 0.3109 gram, and 0.3910 gram of platinum, respectively. Percentages of platinum found are 44.01, 43.80, and 43.87; the percentage required for the formula $2NH_4Cl.PtCl_4$ is 43.9. It has been shown in the preceding paper that the amount of hydriodic acid produced when sodium sulphite reacts with nitrogen iodide is always exactly equivalent to half the amount of sulphite used. Numbers of experiments, which it is not necessary to record, have been made, showing that this result is not affected by the rate at which the sulphite is added or by the consequent appearance or non-appearance of free iodine in the liquid.

The reaction between sodium sulphite and nitrogen iodide

proceeds rapidly and quietly, no bubbles of gas are disengaged if light be excluded, and no other substances besides those mentioned are ever produced. It can, therefore, be used to determine the percentage of nitrogen and of iodine contained in nitrogen iodide.

The ammonia can, of course, be estimated by distilling the product of the action with an excess of caustic potash, but a simpler plan is available. The solution resulting from the action of sodium sulphide upon nitrogen iodide is always found to be acid, since the amount of hydriodic acid produced is greater than that required to neutralize the ammonia simultaneously formed. This excess of acid can easily be estimated by any standard alkali, and since sodium sulphate is neutral and the total amount of hydriodic acid formed is accurately known from the amount of sulphite used, the difference between the amount of hydriodic acid produced and the amount present as free acid represents the amount neutralized by the ammonia formed, and is, consequently, a measure of this. Numbers of experiments have been made to test the accuracy of this method. A quantity of nitrogen iodide was decomposed by a standard solution of sodium sulphite and the free acid present in the resulting solution estimated by a standard solution of baryta. From the amounts of sulphite and of baryta used that of the ammonia formed was calculated. The neutral liquid was then distilled with an excess of caustic potash and the ammonia actually liberated estimated by a standard solution of hydrochloric acid. The results, of which six follow, were in all cases found to be practically identical :

	cc.	cc.	cc.	cc.	cc.	cc.
$\frac{1}{2}\left(\frac{N}{10}\frac{Na_2SO_3}{2}\right) - \left(\frac{N}{10}\frac{Ba(OH)_2}{2}\right)$	20.5	24.1	32.2	17.6	26.4	29.5
N/10 NH_3 obtained by distillation with potash	20.4	24.1	32.2	17.6	26.3	29.5

The standard solutions used in the analysis of nitrogen iodide were decinormal solutions of sodium sulphite, hydro-

chloric acid, barium hydroxide, ammonia, and silver nitrate. They were all standardized either directly or indirectly against the silver nitrate.

The strength of the solution of sodium sulphite was determined by titrating with it an unknown quantity of finely powdered iodine, then estimating the amount of free hydriodic acid produced with standard alkali, and finally the total amount of alkaline iodide formed by standard silver nitrate. The purest sodium sulphite available always contains a small amount of uncombined sodium hydroxide, and consequently, when it is converted by iodine into sodium sulphate the amount of hydriodic acid set free is not quite equal to the total amount formed, the difference being neutralized by the alkali present in the sulphite. When preparing the solution of sodium sulphite, therefore, this small amount of free alkali was neutralized by adding the required quantity of sulphurous acid so that when it reacted with pure iodine exactly its own equivalent of hydriodic acid was set free. The actual analysis is best carried out as follows:

A given quantity of pure nitrogen iodide, either moist or dry, generally from 0.5 to 1 gram, is rinsed into a flask with about 25 cc. of distilled water, and the solution of sodium sulphite slowly run in, light being as far as possible excluded until the particles of nitrogen iodide completely disappear and a yellow or brown liquid containing free iodine is formed. The titration is then finished exactly as with iodine, a few drops of starch solution being used as an indicator. A little litmus is then added to this clear liquid, and the free acid neutralized by either baryta or ammonia. The total iodine present is finally estimated by titration with silver nitrate, using a solution of starch rendered deep blue by iodine as an indicator.

The material analyzed has in every case, except where a special note is made, been purified in the same way. Each specimen was washed by decantation with strong ammonia and, where necessary, allowed to stand under it until all soluble foreign matter was removed. It was then filtered off through asbestos at a pump and well washed, first with tenth-normal ammonia and finally three our four times with dis-

tilled water, which ensures the removal of the last traces of adhering ammonia.

Nitrogen iodide, from whatever source, treated in this way does not render blue a neutral solution of litmus when placed in it, nor give any color to chloroform when shaken with it, and finally, as has been shown in the previous section, half the sulphite titre is always equivalent to the silver titre. The latter is the most delicate test of purity that we have. The slightest decomposition caused by washing or by light is at once detected, as is also the presence of any iodide, iodate, or free iodine.

In calculating the results, the amount of hydriodic acid as given by the sulphite titre has been used. The direct estimation by silver nitrate serves as a check on this sulphite titre as well as a proof that no decomposition of the nitrogen iodide used has taken place during washing or under the influence of light. The results are all given in tabular form, each line representing an analysis. In the first column is given the number of cubic centimeters of a decinormal solution of sodium sulphite $\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ which was found to react with the nitrogen iodide used. The number of cubic centimeters of a decinormal solution of ammonia or other alkali required to neutralize the free hydriodic acid in the resulting solution is given in the second column. The third column contains the number obtained by dividing by 2 the amount of sodium sulphite used; it represents the amount of hydriodic acid produced in the reaction expressed as cubic centimeters of a decinormal solution. In the fourth is stated the number of cubic centimeters of a decinormal solution of silver nitrate which reacted with the hydriodic acid and consequently measures directly the total amount of hydriodic acid formed. The number in this column should agree with that in the third within the limits of experimental error; when this is the case no impurity capable of reacting with either sodium sulphite or silver nitrate can have been present in the nitrogen iodide analyzed, and no decomposition into nitrogen and hydriodic acid can have taken place under the influence of light accidentally admitted during manipulation. The fifth column

contains a number obtained by subtracting the number in the second from that in the third; that is, the amount of free hydriodic acid from the total amount produced. This, therefore, represents the amount of ammonia produced in the reaction.

Now in each analysis

$$\frac{\text{Number in fifth column}}{\text{Number in third column}} = \frac{\text{number of cc. N/10 } NH_3 \text{ produced}}{\text{number of cc. N/10 HI produced}} =$$

$$\frac{\text{Number of molecules of } NH_3 \text{ formed}}{\text{Number of molecules of HI formed}} = \frac{\text{number of atoms of N in the molecule of nitrogen iodide}}{\text{number of atoms of I in the molecule of nitrogen iodide.}}$$

In the sixth column this ratio as actually obtained in each analysis is given, calculated as a certain number of atoms of nitrogen to 3 atoms of iodine. It is found always to be approximately 2 : 3, the variation from this being in every case within the limits of experimental error.

All known methods of preparing nitrogen iodide have been described in a previous paper,[1] the composition of the substance prepared in every one of these ways has been determined.

To avoid all possibility of error, from twenty to sixty concordant analyses of each product have been made; but to save space the results of a few only are given. In most cases these are successive estimations and consequently the average accuracy reached is shown.

Analysis of Nitrogen Iodide Prepared by Adding a Solution of Iodine in Potassium Iodide to a Solution of Ammonia.

The last traces of potassium and ammonium iodide are removed only with difficulty from nitrogen iodide prepared in this way. It is well, therefore, before analysis to allow the product to stand under an excess of 3N-ammonia for a week or so, decanting off and replacing the ammonia solution each day.

[1] "Preparation and Properties of the So-called Nitrogen Iodide": This JOURNAL, **23**, 363.

The compound used in analyses 1, 2, and 3 was prepared by adding a decinormal solution of iodine in potassium iodide to a saturated solution of ammonia.

A number of estimations were made to determine whether the concentration of the iodine solution used in the preparation affects the ratio of nitrogen to iodine in the product. The nitrogen iodide used in analyses 4, 5, and 6 was prepared exactly as before except that a normal solution of iodine in potassium iodide was employed.

Number of analysis.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$.	$\frac{N}{10}$ NH_3 required to neutralize solution = $\frac{N}{10}$ HI produced in free state = a.	$\frac{1}{2}\left(\frac{N}{10}\frac{Na_2SO_3}{2}\right)$ = $\frac{N}{10}$ HI produced = b.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed.	$\frac{N}{10}$ NH_3 formed = $\frac{b-a}{3}$.	Ratio between NaI in molecule of nitrogen iodide $\frac{x}{3} = \frac{b-a}{b}$.
	cc.	cc.	cc.	cc.	cc.	
1	52.4	8.7	26.2	26.2	17.5	2 : 3
2	39.2	6.5	19.6	19.6	13.1	2 : 3
3	77.2	12.9	38.6	38.7	25.7	1.99 : 3
4	40.8	6.8	20.4	20.5	13.6	2 : 3
5	48.0	7.9	24.0	24.0	16.1	2.01 : 3
6	46.6	7.8	23.3	23.3	15.5	1.99 : 3

The concentration of the iodine solution is seen to have no effect whatever upon the composition of the nitrogen iodide. Exactly similar results have been obtained with specimens of nitrogen iodide prepared by the action of solutions of iodine in chloroform and carbon tetrachloride upon ammonia. In both cases the ratio of the number of nitrogen atoms to the number of iodine atoms in the molecule is 2 : 3.

Analysis of Nitrogen Iodide Prepared by the Action of a Strong Solution of Ammonia upon Solid Iodine.

The reaction here is much slower than when dissolved iodine is used as the particles become superficially coated with nitrogen iodide which protects them to some extent from further action. To ensure that no iodine remained unattacked the nitrogen iodide thus prepared was allowed to stand for two months under strong (0.880) ammonia, the latter being frequently decanted off and replaced by fresh. The nitrogen iodide used in analyses 1, 2, and 3 was made from finely di-

vided solid iodine, obtained by precipitating a saturated solution of iodine in potassium iodide by excess of water. That used in 4, 5, and 6 was made from very finely powdered iodine.

Number of analysis.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$.	$\frac{N}{10}$ NH_3 required to neutralize solution = $\frac{N}{10}$ HI produced in free state.	$\frac{1}{2}\left(\frac{N\ Na_2SO_3}{10}\right) = \frac{N}{10}$ HI formed.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed.	$\frac{N}{10}$ NH_3 formed.	Ratio between N and I in molecule of nitrogen iodide.
	cc.	cc.	cc.	cc.	cc.	
1	47.0	7.8	23.5	23.6	15.7	2 : 3
2	52.1	8.9	26.05	26.0	17.35	1.99 : 3
3	38.2	6.5	19.1	19.2	12.6	1.97 : 3
4	39.9	6.8	19.95	20.0	13.15	1.97 : 3
5	29.4	5.0	14.7	14.8	9.7	1.98 : 3
6	35.2	5.9	17.6	17.7	11.7	1.99 : 3

Analysis of Nitrogen Iodide Prepared by the Action of an Alcoholic Solution of Iodine upon Ammonia.

Experiments were next made with the nitrogen iodide which is obtained, mixed with more or less iodoform, whenever iodine dissolved in alcohol is allowed to act upon ammonia dissolved either in water or alcohol. The analysis of the nitrogen iodide contained in this mixture, if it be washed free from alcohol and soluble impurities, can be carried out as though the iodoform were not present, for this is not appreciably attacked during the titrations. The material used in analyses 1, 2, and 3 was prepared by adding a saturated alcoholic solution of iodine to strong aqueous ammonia. It smelled strongly of iodoform, and yellow crystals of this compound were seen floating in the colorless liquid obtained after titration with sodium sulphite. Analyses 4, 5, and 6 were performed with nitrogen iodide obtained by adding a cooled saturated solution of iodine in absolute alcohol to cooled anhydrous alcohol saturated with dry ammonia. It was very carefully washed, using a filter-pump, first with alcoholic ammonia, then with cool alcohol, and finally rapidly with water.

Number of analysis.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$.	$\frac{N}{10}$ NH_3 required to neutralize solution = $\frac{N}{10}$ HI produced in free state.	$\frac{1}{2}\left(\frac{N\ Na_2SO_3}{10}\right) = \frac{N}{10}$ HI formed.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed.	$\frac{N}{10}$ NH_3 formed.	Ratio between N and I in molecule of nitrogen iodide.
	cc.	cc.	cc.	cc.	cc.	
1	61.3	10.3	30.65	30.7	20.35	1.99 : 3
2	51.3	8.8	25.65	25.6	16.95	1.98 : 3
3	46.4	8.0	23.2	23.3	15.2	1.96 : 3
4	63.3	10.5	31.65	31.7	21.15	2 : 3
5	40.0	6.7	20.0	20.1	13.3	1.99 : 3
6	29.6	4.9	14.8	14.9	9.9	2 : 3

It is seen that the ratio of nitrogen to iodine in nitrogen iodide produced in this way, although it is never obtained quite free from foreign matter, is the same as in nitrogen iodide prepared by other methods.

Analysis of Nitrogen Iodide Prepared by Adding Ammonia to a Solution of Potassium Hypoiodite Containing an Excess of Potash.

Either amorphous or crystalline nitrogen can be produced at will by this reaction according to the concentration of the potassium hypoiodite in the solution used. When the concentration of the hypoiodite is above a certain limit the compound is formed so rapidly that it cannot assume the crystalline form.

Analyses 1, 2, and 3 were made using amorphous nitrogen iodide prepared thus.

When the concentration of the hypoiodite is above the limit at which nitrogen iodide is first produced and below the limit at which it separates in an amorphous state, it assumes a crystalline form, the size and perfection of the crystals being greater the slower the rate of deposition.

Analyses 4, 5, and 6 were made with finely crystallized nitrogen iodide obtained in this way.

Number of analysis.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$. cc.	$\frac{N}{10}$ NH_3 required to neutralize solution $=\frac{N}{10}$ HI produced in free state. cc.	$\frac{1}{2}\left(\frac{N}{10}\frac{Na_2SO_3}{2}\right)=\frac{N}{10}$ HI formed. cc.	$\frac{N}{10}$ $AgNO_3$ required $=\frac{N}{10}$ HI formed. cc.	$\frac{N}{10}$ NH_3 formed. cc.	Ratio between N and I in molecule of nitrogen iodide.
1	43.8	7.3	21.9	21.9	14.6	2 : 3
2	39.5	6.6	19.75	19.8	13.15	1.99 : 3
3	48.9	8.1	24.45	24.5	16.35	2 : 3
4	55.9	9.3	27.95	28.0	18.65	2 : 3
5	63.6	10.6	31.8	31.8	21.2	2 : 3
6	94.6	15.8	47.3	47.3	31.5	1.99 : 3

The relation between the nitrogen and iodine in the substance obtained by this method is seen to be the same whether it is amorphous or crystalline, and to be identical with the relation invariably found.

Analysis of Nitrogen Iodide Prepared by the Action of Iodine Monochloride on Ammonia and of Nitrogen Iodide Obtained by the Interaction of Calcium Hypochlorite and Ammonium Iodide.

A precisely similar result was obtained in analyses 1, 2, and 3 of the following table, in which amorphous nitrogen iodide obtained by adding a decinormal solution of iodine monochloride in dilute hydrochloric acid to a 3N-solution of ammonia was employed.

Analyses 4, 5, and 6 were made with crystalline nitrogen iodide obtained by dissolving the above in hot ammonia solution and cooling the liquid. This apparent recrystallization must be very rapidly performed and consequently only a very small amount of nitrogen iodide can be obtained thus at a time. If too long a period be taken either in heating the solution or in cooling it, much ammonium iodate is produced but little or no crystalline nitrogen iodide.

It is seen that the relation between the nitrogen and iodine in the compound is not affected by this apparent recrystallization.

The nitrogen iodide used in analyses 7, 8, and 9 was made by adding an excess of a clear solution of bleaching-powder

to a solution of ammonium iodide. Nitrogen iodide is precipitated mixed with a variable amount of calcium iodate, the last traces of which are difficult to remove. The material analyzed was freed from this substance by thoroughly washing with decinormal ammonia. The relation of nitrogen to iodine was found to be the same as in nitrogen iodide prepared in any other way.

Number of analysis.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ cc.	$\frac{N}{10}$ NH_3 required to neutralize solution = $\frac{N}{10}$ HI produced in free state. cc.	$\frac{1}{2}\left(\frac{N}{10}\frac{Na_2SO_3}{2}\right) = \frac{N}{10}$ HI formed. cc.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed. cc.	$\frac{N}{10}$ NH_3 formed. cc.	Ratio between N and I in molecule of nitrogen iodide.
1	171.2	28.5	85.6	85.5	57.1	2 : 3
2	128.4	21.4	64.2	64.2	42.8	2 : 3
3	165.5	27.6	82.75	82.8	55.15	1.99 : 3
4	61.5	10.3	30.75	30.7	20.45	1.99 : 3
5	66.9	11.1	33.45	33.5	22.35	2 : 3
6	80.2	13.4	40.1	40.2	26.7	1.99 : 3
7	36.2	6.0	18.1	18.2	12.1	2 : 3
8	39.2	6.6	19.6	19.8	13.0	1.98 : 3
9	30.4	5.1	15.2	15.3	10.1	1.99 : 3

Composition of the So-called "Nitrogen Iodide."

All the preceding results show that the relation by weight between the nitrogen and iodine in the various specimens of nitrogen iodide analyzed does not vary either with the mode of preparation or the state of aggregation of the compound, and that this relation is 2 : 3 when expressed in terms of the atomic weights of the two elements.

The reactions in which the compound is formed are, moreover, essentially the same. They all lead to the production of ammonium hypoiodite, from which it is produced by a reversible change. We have, therefore, every ground for concluding that only one such compound exists, and that in its molecule 2 atoms of nitrogen are associated with 3 atoms of iodine.

Now it is shown in the following paper that when nitrogen iodide is exposed to sunlight it breaks up quantitatively into nitrogen and hydriodic acid. This proves that the molecule

of the compound contains only nitrogen, hydrogen, and iodine atoms and that each atom of iodine is associated with 1 atom of hydrogen. Therefore, since the foregoing analyses have shown that in nitrogen iodide 2 nitrogen atoms are associated with 3 iodine atoms and, since the decomposition by light shows that these latter are associated with 3 hydrogen atoms, the simplest formula which expresses its composition is $N_2H_3I_3$. The correctness of this conclusion has been confirmed by the analysis of weighed quantities of the dry compound.

Analysis of Weighed Quantities of Nitrogen Iodide.

Nitrogen iodide so readily undergoes decomposition that it is somewhat difficult to obtain it free from moisture in a state of purity. It can, however, be dried without change over lime or baryta in an atmosphere of ammonia if light be entirely excluded. A number of analyses of weighed amounts of nitrogen iodide have consequently been made.

The following procedure was adopted: Nitrogen iodide was thoroughly washed with strong ammonia and allowed to drain. From 0.5 to 1 gram of this moist material was then spread in a thin layer on a weighed watch-glass and exposed for several days in an atmosphere of pure ammonia over baryta till its weight was constant. It was then placed for a very short time over sulphuric acid in a vacuum to remove traces of ammonia gas, and finally was weighed, detached from the watch-glass after moistening with water, and analyzed as previously described. The operations were conducted in a cool cellar and light, except that from a small gas flame during transference and weighing, was entirely excluded. The nitrogen iodide must be placed very loosely on the watch-glass; if it be pressed into a compact mass before drying it almost always explodes during titration with the sulphite. This is dangerous, as the explosion of not more than 0.01 part of a gram suspended in water is sufficient to shatter a stout flask.

A considerable number of such analyses of dry nitrogen iodide prepared in different ways have been made. The ratio between the ammonia and hydriodic acid produced is exactly the same as when the moist substance is employed and the percentages of nitrogen and iodine agree with those required by

the formula $N_3H_3I_3$, which may thus be considered as definitely established.

The results are recorded exactly as before, except that in the first column the weight of dry nitrogen iodide used is given, while in two additional columns, 8 and 9, the percentages of nitrogen and iodine, respectively, are given.

Analyses 1, 2, and 3 were made with nitrogen iodide prepared by the action of a strong solution of ammonia on pure precipitated iodine. Those numbered 4, 5, and 6 with finely crystalline nitrogen iodide obtained by adding ammonia to a solution of potassium hypoiodite, while that used in 7 and 8 was made by taking amorphous nitrogen iodide prepared from iodine monochloride and recrystallizing it by heating it with strong ammonia and rapidly cooling the solution.

The formula $N_3H_3I_3$ requires 92.44 per cent of iodine, 6.82 per cent of nitrogen, and 0.73 per cent of hydrogen (I = 126.85, N = 14.04, H = 1.01).

Number of analysis.	Weight of nitrogen iodide used.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$. $\frac{N}{10}$ NH_3 required to neutralize solution =	$\frac{N}{10}$ HI produced in free state. $\frac{1}{2}\left(\frac{N}{10}\ Na_2SO_3\right) = \frac{N}{10}$ HI formed.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed.	$\frac{N}{10}$ NH_3 formed.	Ratio between N and I in molecule of nitrogen iodide.	Percentage of iodine obtained.	Percentage of nitrogen obtained.
	Gram.	cc.	cc.	cc.	cc.			
1	0.5937	86.5	14.5	43.25	43.3	28.75	1.99 : 3	92.41	6.80
2	0.2733	39.8	6.7	19.9	19.9	13.2	1.99 : 3	92.36	6.78
3	0.3794	55.4	9.2	27.7	27.7	18.5	2 : 3	92.61	6.85
4	0.3758	54.8	9.1	27.4	27.4	18.3	2 : 3	92.49	6.84
5	0.3774	55.0	9.2	27.5	27.4	18.3	1.99 . 3	92.43	6.81
6	0.3378	49.2	8.2	24.6	24.7	16.4	2 : 3	92.38	6.82
7	0.4156	60.5	10.1	30.25	30.3	20.15	1.99 : 3	92.33	6.81
8	0.3075	44.8	7.5	22.4	22.4	14.9	1.99 : 3	92.40	6.80

Experiments made to Determine whether Similar Substances of Composition Differing from $N_3H_3I_3$ Could Be Produced.

The preceding investigation has shown that in all reactions which yield nitrogen iodide the substance produced is a single definite compound, the composition of which is represented by the formula $N_3H_3I_3$. The results of previous ob-

servers have, however, differed so widely that it seemed conceivable that other substances might be produced in the reactions, although, under the conditions employed, these had never been obtained. Consequently, experiments were made to determine whether any other substance could be produced, but in every case with a negative result. A number of analyses, which it is not necessary to record, were first made to determine whether the compound had the same composition at the instant of its formation as after standing for a considerable time under ammonia. It was found that the ratio of nitrogen to iodine in the compound is exactly the same at the moment of its formation as after standing for months under strong ammonia.

A number of experiments have been made to decide whether nitrogen iodide can combine, however loosely, with ammonia as it is conceivable, though improbable, that such an unstable compound might be decomposed by the water used to remove the last traces of adhering ammonia. Nitrogen iodide prepared by adding a decinormal solution of iodine in potassium iodide to ammonia, after thoroughly washing, was allowed to stand for two months under 0.880 ammonia; it was then filtered off, well washed with strong ammonia, and finally twice with decinormal ammonia; the mass was then pressed dry between filter-paper, and small pieces from the middle taken for analysis.

Experiments 1, 2, and 3 in the following table give the results. The ratio between nitrogen and iodine is practically the same as before, the nitrogen being very slightly too high owing to traces of ammonia adhering to the damp mass.

Further experiments were made with the same object, a slightly different method being adopted. Amorphous nitrogen iodide, after standing under 0.880 ammonia for two months, was thoroughly washed with strong ammonia, and the pulp thus obtained mixed with distilled water. After subsidence, 25 cc. of the lower layer containing suspended nitrogen iodide was removed and titrated as usual. Some of the supernatant liquid was then filtered off and the ammonia per cubic centimeter estimated.

Assuming that amorphous nitrogen iodide has the same

specific gravity as crystalline, the volume occupied by it can be calculated from the sulphite titre and, deducting this from the 25 cc. of liquid taken, we obtain the volume of the ammonia solution in which it was suspended, we also know how much ammonia this contains. Subtracting the amount from the total quantity found in the estimation, that yielded by the nitrogen iodide is obtained. We thus find the relation between the ammonia and hydriodic acid, yielded by nitrogen iodide which has never been removed from a solution of ammonia. This is found to be precisely the same as in the washed specimens.

The ammonia solution in which the nitrogen iodide was finally suspended was always diluted to such a point that the product of the titration with sulphite was slightly acid. For clearness the details are stated as in previous tables, the amount of ammonia present in the solution suspending the nitrogen iodide being added to that required to neutralize the liquid obtained after titration with sodium sulphite.

The results given in experiments 4, 5, and 6 show conclusively that the molecule of nitrogen iodide is unable to combine with ammonia in aqueous solution.

Number of analysis.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$.	$\frac{N}{10}$ NH_3 required to neutralize solution $= \frac{N}{10}$ HI produced in free state.	$\frac{1}{2}\left(\frac{N}{10}\frac{Na_2SO_3}{2}\right) = \frac{N}{10}$ HI formed.	$\frac{N}{10}$ $AgNO_3$ required $= \frac{N}{10}$ HI formed.	$\frac{N}{10}$ NH_3 formed.	Ratio between N and I in molecule of nitrogen iodide.
	cc.	cc.	cc.	cc.	cc.	
1	97.8	16.2	48.9	48.9	32.7	2.006 : 3
2	97.0	16.1	48.5	48.6	32.4	2.004 : 3
3	85.1	14.1	42.55	42.5	28.45	2.005 : 3
4	83.8	14.0	41.9	42.0	27.9	1.99 : 3
5	97.8	16.3	48.9	48.9	32.6	2 : 3
6	69.0	11.7	34.5	34.4	22.8	1.98 : 3

The methods of preparing nitrogen iodide and the actions which result when it is treated with potash or ammonia prove that the hypoiodites have no action upon the compound.

Experiments have also been made which show that iodine itself is neither able to combine with the substance nor to replace the hydrogen atoms contained in the molecule.

When nitrogen iodide is digested for some hours with a solution of iodine, it apparently suffers no change but, on filtering off and washing, a little iodine is found to be retained, apparently deposited upon the solid particles. That no combination has taken place is proved by the fact that a very small and variable quantity only is thus attached, and by the fact that it can be recognized as iodine by its smell and by shaking with chloroform. The amount of this retained iodine can be estimated by taking advantage of two circumstances: first, that all the iodine present as nitrogen iodide oxidizes double the amount of sodium sulphite that it would were it present as the free element, while any iodine present as such simply oxidizes its equivalent; and second that silver nitrate estimates the total amount of hydriodic acid produced, and gives the same result whether the iodine originally replaced hydrogen or was present in the free state.

If a be the number of cubic centimeters of decinormal sodium sulphite which reacts with a given quantity of such a mixture of free iodine and of nitrogen iodide, either with its hydrogen replaced by iodine or not, and if b represent the number of cubic centimeters of decinormal silver nitrate required to react with the hydriodic acid produced, then if x be the amount of iodine present as nitrogen iodide, and if y be the amount present in the free state measured in cubic centimeters of a decinormal solution, we have:

$$a = 2x + y, \qquad b = x + y,$$

whence we have

$$x = a - b \qquad \text{and} \qquad y = 2b - a.$$

The experiments were carried out as follows: Nitrogen iodide was shaken up with an excess of a decinormal solution of iodine in potassium iodide and left for six hours, all light being excluded. At the end of that time the substance was filtered off, washed with water, and titrated as usual.

In the reaction of the product with the sodium sulphite all the ammonia liberated must come from the nitrogen iodide and, since the amount of free hydriodic acid is known from the alkali titre, and the total amount of hydriodic acid pro-

duced from the silver nitrate titre, the difference between the two, as before, gives the amount.

We know, therefore, the amount of nitrogen and can calculate x, that is the amount of iodine associated with it. We thus obtain the relation between the nitrogen and the iodine contained in the product, and this is found to be approximately 2 : 3, exactly as before treatment with the iodine. This proves that iodine has no substituting or other action on nitrogen iodide. Very large amounts were titrated each time to ensure accuracy. Experiments 1, 2, and 3 were made with amorphous nitrogen iodide prepared by digesting finely divided precipitated iodine for two months with strong ammonia, while in 4, 5 and 6 crystalline nitrogen iodide was used.

Number of analysis.	$\frac{N}{10}\frac{Na_2SO_3}{2} = a$. cc.	$\frac{N}{10}$ NH_3 required to neutralize solution = $\frac{N}{10}$ HI produced in free state. cc.	$\frac{N}{10}$ $AgNO_3$ required = $\frac{N}{10}$ HI formed = b. cc.	$\frac{N}{10}$ NH_3 formed. cc.	$x = \frac{N}{10}$ iodine present as nitrogen iodide. cc.	$y = \frac{N}{10}$ iodine present as free element. cc.	Percentage of total iodine present as free element. cc.	Ratio between N and I in nitrogen iodide after treatment with iodine.
1	210.5	37.9	106.8	68.5	103.7	3.1	2.9	1.98 : 3
2	227.4	40.4	115.3	74.9	112.1	3.2	2.77	2 : 3
3	250.1	45.6	126.9	81.6	123.2	3.7	2.91	1.98 : 3
4	230.1	42.0	117.1	75.1	113.0	4.1	3.50	1.99 : 3
5	192.4	35.1	97.8	62.7	94.6	3.2	3.27	1.98 : 3
6	381.9	69.7	194.3	124.6	187.6	6.7	3.44	1.99 : 3

Discussion of Previously Published Analyses.

In the preceding pages it is shown that the same substance is formed in all reactions which are known to yield nitrogen iodide, and that this is a definite compound whose composition is represented by the formula $N_3H_3I_3$. The statement that a number of distinct substances can be produced in these reactions, although so generally accepted, is thus shown to be inaccurate. The analytical results upon which alone this statement is based must, therefore, be faulty or the substances analyzed must have been impure or partially decomposed by the treatment preceding or during analysis.

These analyses have been made with unknown weights of material, and consequently only the ratio between the contained iodine and nitrogen determined, the formulæ being deduced from this on the assumption, which we elsewhere show to be erroneous, that nitrogen iodide is formed from ammonia by substitution.

Bineau, in 1845, first attempted to analyze the substance, making three estimations of the amounts of ammonium iodide and hydriodic acid produced when it is decomposed by hydrogen sulphide.

Gladstone, seven years later, published two analyses, using Bineau's method in one and the decomposition of the compound by sulphurous acid in the other. His results are similar to Bineau's, the ratio obtained being roughly 1 : 2. Bunsen, in the same year, published two analyses, using the decomposition by hydrogen chloride. He obtained the ratios N : I (2.04 : 3) and (4 : 11.9) in specimens prepared differently. These numbers of Bunsen, which did not agree at all with his own, caused Gladstone, still employing sulphurous acid, to publish four more analyses which, although differing among themselves by nearly 9 per cent, roughly confirmed his previous estimations. Stahlschmidt, ten years later, in seven analyses obtained ratios of nitrogen to iodine varying according to the mode of preparation from 1 : 1.21 to 1 : 2.98. Mallet, in 1879, then published some analyses of nitrogen iodide which, in most cases, he washed with alcohol, a liquid which very rapidly decomposes it. He obtained varying ratios, such as 1 : 2.94, 1 : 2.47, and 1 : 2.13. Raschig, in 1885, in consequence of the very contradictory results hitherto obtained, endeavored, but unsuccessfully, to prepare pure substances corresponding to the formulæ hitherto suggested; he obtained discrepant results and states at the end of his paper that the question of the composition must still be regarded as an open one. Since then Szuhay published some numbers, in 1893, but they may be disregarded, as he prefaces his work by the statement that he has convinced himself that by the action of iodine on ammonia no other substances besides nitrogen iodide and ammonium iodide are produced.

On considering the work of all these chemists, several

things appear noteworthy. In the few cases where more than one analysis of the same material is published the results differ far more than can be accounted for by experimental error, while substances of very different compositions are obtained by reactions essentially the same.

The methods of analysis, again, which have been employed cannot have given accurate results for, as we show in other papers, when hydrogen sulphide, sulphurous acid, or hydrochloric acid acts upon nitrogen iodide, the whole of the nitrogen is not obtained as ammonia but a considerable and variable amount is liberated as gas. Further, no precaution, apparently, has ever been taken to exclude light during the operations.

These facts would account for many discrepancies and a further source of error is found in the readiness with which the compound is decomposed if washed too long before analysis.[1] Several years ago, on first taking up its study, specimens of nitrogen iodide prepared in various ways were analyzed, the material being washed, as recommended by previous observers, till the alkaline reaction of the filtrate disappeared or was marked by the liberation of iodine. The numbers obtained were not sufficiently concordant to justify their publication, but they gave a ratio between the nitrogen and iodine atoms approximately 1 : 2. A very large number of analyses were afterwards made to see if close agreement between the results could not be obtained, and the present research is the outcome. It was first found that neither sodium thiosulphate, hydrogen sulphide, nor hydrochloric acid could be used in the analyses,—the thiosulphate because irregular oxidation was liable to take place, and hydrogen sulphide and hydrochloric acid because they always caused the liberation of a small and variable amount of nitrogen.

It was next discovered that even diffused light must be excluded during the operations,[2] and finally, that any prolonged washing with water causes a very noticeable decomposition. To obtain accurate results it is necessary before analysis to

[1] Compare "Action of Reducing Agents upon Nitrogen Iodide," this JOURNAL, 23, 369.

[2] *Ibid.*

wash the compound thoroughly with decinormal ammonia, and finally to remove any traces of this adhering to the solid by rapidly washing three or four times with pure water. In the material so treated neither ammonia nor iodine is present and the amount of any reducing agent oxidized by it is exactly double the quantity equivalent to the iodine it contains. If the washing be continued beyond this point, the filtrate becomes slightly alkaline and colored yellow by iodine, iodine can be recognized in the solid mass, and the amount of any reducing agent oxidized is less than double the amount equivalent to the contained iodine.

It is very probable that the three causes, unsuitable reaction, decomposition by light during manipulation, and decomposition by prolonged washing, adequately account for the varying results, because in every analysis yet recorded, except a single one of Bunsen's, less than 2 atoms of nitrogen have been found associated with 3 atoms of iodine, as would be the case if any or all of these causes were operative. Since single analyses only have, as a rule, been made of specimens prepared in different ways, chemists have concluded that they had in their hands distinct, but similar, substances of definite composition. Mixtures of any composition from nitrogen iodide, $N_2H_3I_3$, to pure iodine can, in fact, be obtained by washing nitrogen iodide continuously. To show this, about a kilogram of nitrogen iodide was taken, placed in a funnel closed by a plug of asbestos, and a slow stream of distilled water allowed to percolate through the mass; every few hours a portion was removed, rapidly washed by water, and analyzed. The amount of nitrogen associated with a given weight of iodine was found gradually, but absolutely continuously, to become less and less until at the end of several weeks only a small quantity of pure iodine remained. Obviously, if only a few analyses were made, mixtures of any possible composition containing less nitrogen than $N_2H_3I_3$ might be obtained and might be assumed, in the absence of evidence to the contrary, to be definite substances.

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THE ACTION OF LIGHT ON NITROGEN IODIDE.

By F. D. Chattaway and K. J. P. Orton.

Guyard, who first studied the decomposition of nitrogen iodide by light in the presence of water and ammonia, found that diffused light caused a slow evolution of nitrogen, while direct sunlight brought about a rapid effervescence. On account of its extreme sensitiveness he suggested forms of photometers in which nitrogen iodide was employed. He states that the products of the decomposition are nitrogen, ammonium iodide, and traces of ammonium iodate, and writes the following equation to express the reaction :

$$6NH_3I + 4NH_4OH = 6NH_4I + 4N + 4H_2O.$$

Though the results are nowhere given, he remarks that his actual experimental numbers agree rather with the atomic ratio (10 : 7) for iodine to nitrogen than with the ratio (3 : 2) required by the above equation. He does not say whether, in obtaining this ratio (10 : 7), he considers only the iodine present as iodide or the total iodine as iodide and iodate, in fact he has left no record of any estimation of iodate.

Guyard also describes the action of light on iodine suspended in ammonia solution and mentions that from 1.27 grams of iodine 33.5 cc. of nitrogen were evolved. This is the only instance in which he gives numerical data.

Having obtained nitrogen iodide of a definite and known composition we have investigated the action of light upon it. When nitrogen iodide suspended in a solution of ammonia is exposed to light, nitrogen is evolved and the solid disappears, while ammonium iodide and ammonium iodate are formed in the liquid. The quantity of the latter is never negligible, although it varies within wide limits. It is, moreover, formed from ammonium hypoiodite, which is the first product of the action, and can always be recognized in the solution during the decomposition.

These substances are formed in two reactions which go on simultaneously, one, a simple decomposition caused by light, the other, an action which goes on equally well in the dark,

due to the ammonia solution in which the nitrogen iodide is suspended.

The main reaction is the simple one. Under the influence of light the nitrogen iodide breaks down quantitatively into nitrogen and hydriodic acid, thus:

$$N_2H_3I_3 = N_2 + 3HI.$$

The ammonia present apparently only affects this action by combining with the hydriodic acid formed, and so preventing further secondary reactions.

While this decomposition is taking place a variable amount of the nitrogen iodide is hydrolyzed, the ammonium hypoiodite so formed being slowly transformed into ammonium iodide and ammonium iodate, thus:

$$N_2H_3I_3 + 3H_2O = 2NH_3 + 3HIO;$$
$$3HIO + 3NH_3 = 3NH_4IO = NH_4IO_3 + 2NH_4I.$$

The amount of hydrolysis varies with the temperature and the length of time required for the decomposition. Usually, on a bright, sunny day, from 2–4 per cent only is hydrolyzed while as high a percentage as 25 has been observed when the day has been dull and the decomposition consequently very slow.[1]

The action of light on iodine suspended in ammonia is really an action on nitrogen iodide itself. We prove later that in the interaction of iodine and ammonia half the iodine becomes ammonium iodide and half ammonium hypoiodite, which for the most part decomposes into nitrogen iodide. The latter then reacts exactly as when it is previously prepared and suspended in ammonia.

Similar actions take place if the nitrogen iodide is suspended in water; but in this case a further complication is introduced by the action of the hydriodic acid produced on the still undecomposed nitrogen iodide,[2] a fact entirely overlooked by Guyard.

[1] Guyard says that he found the atomic ratio of iodine to nitrogen 10:7. In certain of our experiments the total iodine (as iodide and iodate) present, after the decomposition was complete, bore to the nitrogen evolved the ratio 10:7. Such is the case when 4 per cent of the nitrogen iodide has been hydrolyzed. Obviously, therefore, Guyard did not estimate the iodate separated, and consequently missed its significance.

[2] In an article to be published later it will be shown that nitrogen iodide and hydriodic acid read thus: $N_2H_3I_3 + 5HI = 2NH_4I + 3I$.

Dry nitrogen iodide also is rapidly decomposed by light, nitrogen being evolved while free iodine and ammonium iodide are formed. Here also the first action, without doubt, is the simple decomposition into nitrogen and hydriodic acid; the latter then reacts with the still undecomposed solid, forming iodine and ammonium iodide. [1]

The explosive decomposition of nitrogen iodide caused by heat or percussion is probably also a sudden resolution into nitrogen and hydriodic acid similar to the slow decomposition caused by light. The iodine liberated may be formed either by decomposition of the hydriodic acid at the high temperature of the explosion or by its action on a portion of the original material. If such an explosion be closely watched, a white fume of hydrogen iodide can always be seen surrounding the mass of violet iodine vapors formed.

EXPERIMENTAL PART.

A preliminary experiment was made to determine the substances formed in the decomposition of nitrogen iodide by light. About 2 grams of the pure iodide were shaken up with 200 cc. of 5N-ammonia solution and exposed to diffused light in a flask arranged so that the gas evolved could be collected. Throughout the decomposition nothing but nitrogen was given off. The supernatant liquor became of a very faint yellow color. Fifty cc. were removed, filtered through asbestos, and titrated with standard sodium arsenite, which is oxidized by hypoiodite but not by iodate.[1] One cc. of tenth-normal arsenite was oxidized. When the whole of the iodide had disappeared the ammonia was boiled off, after adding caustic potash, and the iodate and iodide estimated. On acidifying with dilute sulphuric acid, the iodine which was set free was titrated with standard sodium sulphite. Then the total iodine (now all present as hydriodic acid) was estimated by a tenth-normal solution of silver nitrate. 21.1 cc. of tenth-normal sodium sulphite and 112.2 cc. tenth-normal silver nitrate were required. Now one-sixth of the sulphite titre represents iodine as iodate, and three times the iodine as iodate equals the total

[1] Lonnes (Ztschr. anal. Chem., 33, 409), in a valuable and exhaustive paper on the titration of iodine by solutions of arsenite, has shown that the latter is oxidized by hypoiodite and not by iodate.

iodine (as iodide and iodate) formed by hydrolysis of nitrogen iodide (see equations given above). Therefore 10.55 cc. of a tenth-normal solution of iodine (*i. e.* one-half the sulphite titre) represents the amount of iodine in the nitrogen iodide which has been hydrolyzed, while 112.2 cc. represent the total amount of iodine in the nitrogen iodide used. The percentage of nitrogen iodide hydrolyzed is $\frac{10.55 \times 100}{112.2} = 9.4$. No other substances besides nitrogen, ammonium iodide, hypoiodite, and iodate were formed.

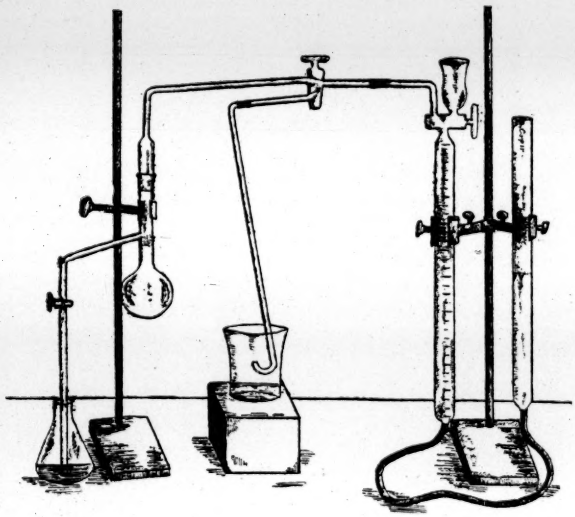
Estimation of Each Substance Produced when Nitrogen Iodide, Suspended in a Solution of Ammonia, Decomposes under the Influence of Light.

It is obvious from the above experiment that the hydrolysis which accompanies the decomposition by light cannot be neglected. In the following experiments each product was estimated; *viz.*, nitrogen, ammonium iodide, and ammonium iodate. The decomposition was effected in the apparatus shown in the illustration.

A round-bottomed flask of 150 cc. capacity was ground on to a tube sealed to one limb of a three-way tap. This tap was connected by its second limb with a Lunge's nitrometer, and by its third to a delivery tube by which the nitrogen collected in the nitrometer could be transferred to a graduated tube standing over water, and measured.

In the experiments, crystalline nitrogen iodide was thoroughly washed and placed in the flask under a solution of 3N-ammonia. Air was displaced from the apparatus by drawing in more ammonia solution by the side-tube. It was found necessary to place a plug of asbestos in the tube just above the neck of the flask to prevent small particles of nitrogen iodide attached to bubbles of nitrogen being carried over into the nitrometer during the evolution of gas.

As soon as the air was displaced the flask was exposed to bright sunlight, which was also reflected on to the nitrogen iodide by a large concave mirror. Under these conditions two hours were generally sufficient for complete decomposition.



When all the nitrogen iodide had disappeared the nitrogen was driven over into the measuring tube and its volume determined, while the liquid in which it had decomposed and the washings of the connecting tube were collected and analyzed as described above. The total iodine (*i. e.* the silver nitrate titre) less the iodine, as iodide and iodate formed by hydrolysis (*i. e.* half the sulphite titre), measures the amount of hydriodic acid formed in the decomposition of nitrogen iodide into nitrogen and hydriodic acid. The results of five experiments are given in the following table. In the fourth column are numbers obtained by subtracting those in the second from those in the third. They give as cubic centimeters of a tenth-normal solution the amount of hydriodic acid formed from the nitrogen iodide, which has been decomposed into nitrogen and hydriodic acid. In the fifth column is given the number of cubic centimeters of nitrogen at normal temperature and pressure calculated from this hydriodic acid

which should be obtained, supposing that the nitrogen iodide breaks up according to the equation

$$N_2H_3I_3 = N_2 + 3HI.$$

In the sixth column is given the number of cubic centimeters of nitrogen actually measured.

(The mass of 1 cc. of nitrogen at 0° and 760 mm. is taken as 0.00125 gram.)

$\frac{N}{10}\frac{Na_2SO_3}{2}$.	$\frac{1}{2}\left\{\frac{N}{10}\frac{Na_2SO_3}{2}\right\} = \frac{N}{10}$ I in nitrogen iodide hydrolyzed.	$\frac{N}{10}\frac{AgNO_3}{1} = \frac{N}{10}$ I in total amount of nitrogen iodide used in experiment.	$\frac{N}{10}\frac{AgNO_3}{1} - \frac{1}{2}\left\{\frac{N}{10}\frac{Na_2SO_3}{2}\right\} = \frac{N}{10}$ HI obtained by decomposition of a portion of nitrogen iodide into hydriodic acid and nitrogen.	Amount of nitrogen that should be obtained at 0° and 760 mm. calculated from hydriodic acid in previous column.	Amount of nitrogen actually measured at 0° and 760 mm.	Percentage of nitrogen iodide hydrolyzed.	Percentage of nitrogen iodide decomposed by light.
cc.	cc.	cc.	cc.	cc.	cc.		
2.96	1.48	43.16	41.68	31.12	30.8	3.42	96.58
2.24	1.12	48.72	47.60	35.54	35.26	2.29	97.71
4.08	2.04	62.63	60.59	45.24	44.61	2.45	97.55
4.08	2.04	55.65	54.11	40.39	39.73	2.76	97.24
7.76	3.88	75.28	71.40	53.31	53.01	3.82	96.18

The agreement is very close, but in every case the amount of nitrogen actually collected is slightly too small.

A loss must, however, necessarily occur because the solution of ammonia used in the reaction flask is saturated at the beginning of the experiment with air at the ordinary atmospheric pressure and consequently with nitrogen at four-fifths of an atmosphere. During the decomposition it becomes saturated with nitrogen at the atmospheric pressure.

Experiment Demonstrating that Hydriodic Acid is Liberated during the Decomposition by Light.

When nitrogen iodide decomposes under the influence of light all the iodine appears as hydriodic acid, which must neutralize an equivalent quantity of the ammonia in which it is suspended. In an experiment performed to demonstrate this conclusion, pure nitrogen iodide was allowed to decompose in light under a known excess of tenth-normal ammonia.

After the disappearance of the nitrogen iodide a known excess of tenth-normal sulphuric acid was added, and the free iodine representing the iodate estimated as usual by standard sulphite. The excess of sulphuric acid was now titrated by standard alkali and finally the total iodine in the nitrogen iodide used by tenth-normal silver nitrate.

$\frac{N}{10}$ NH_3 added.	$\frac{N}{10}$ H_2SO_4 required to neutralize NH_3 left free after the reaction.	$\frac{N}{10}$ NH_3 neutralized in the reaction = a.	$\frac{N}{10}$ Na_2SO_3 required to react with HIO_3 produced in the hydrolysis.	$\frac{N}{10}$ HI formed by action of sodium sulphite on the HIO_3 produced in the hydrolysis $= \frac{1}{6}\left\{\frac{N}{10}\ Na_2SO_3\right\}$	$\frac{N}{10}$ NH_3 neutralized by nitrogen iodide hydrolyzed = b.	$\frac{N}{10}$ $AgNO_3 = \frac{N}{10}$ I in nitrogen iodide used. $\frac{1}{2}\left\{\frac{N}{10}\ Na_2SO_3\right\} =$	$\frac{N}{10}$ HI formed by decomposition of nitrogen iodide in N and HI = $\frac{N}{10}$ NH_3 that should be neutralized.	$(a-b) = \frac{N}{10}$ NH_3 actually neutralized by the HI formed in the decomposition by light.
cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
125.8	104.0	21.8	12.9	2.15	26.3	19.85	19.65	
188.7	156.0	32.7	20.3	3.38	39.6	29.45	29.32	

In column 7 is the amount of ammonia which should be neutralized in the decomposition. It is calculated from the hydriodic acid produced by the action of light. In column 8 is the ammonia actually neutralized. The agreement is sufficiently close. It is noteworthy that the percentages of nitrogen iodide hydrolyzed in these experiments are very high; *viz.*, 24.5 and 25.6. The experiments were made in a warm room in December, and several days elapsed before the nitrogen iodide completely disappeared.

Action of Light on Iodine Suspended in a Solution of Ammonia.

In this experiment we were able to compare our results with the numbers given by Guyard. A weighed quantity of iodine was placed under 150 cc. of 3N-ammonia solution in the apparatus described above, and exposed to direct sunlight or to the light from a Welsbach incandescent burner when the former was not available. After the disappearance of all solid particles the evolved nitrogen was measured and the iodate and total iodine estimated, the latter by weighing as silver iodide.

Weight of iodine used and number of cc. of a $\frac{N}{10}$ I solution corresponding to this.	Half amount of iodine used = amount converted into nitrogen iodide and ammonium hypoiodite as cubic centimeters of a $\frac{N}{10}$ I solution.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$	$\frac{1}{2}\left(\frac{N}{10}\ Na_2SO_3\right) = \frac{N}{10}$ I in nitrogen iodide hydrolyzed and in ammonium hypoiodite.	$\frac{1}{2}\left(\frac{N}{10}\ I\ used\right) - \left(\frac{N}{10}\ \frac{Na_2SO_3}{2}\right)$ $= \frac{N}{10}$ I obtained by decomposition of a portion of the nitrogen iodide formed into hydriodic acid and nitrogen.	Amount of nitrogen that should be obtained calculated from amount of hydriodic acid produced as given in previous column at 0° and 760 mm.	Amount of nitrogen actually measured at 0° and 760 mm.
Gram. cc.	cc.	cc.	cc.	cc.	cc.	cc.
1.1486 = 90.8	45.4	7.6	3.8	41.6	31.05	30.45

The agreement between the numbers in columns 6 and 7 is satisfactory and proves the correctness of the interpretation given above.

Action of Light of Different Wave-lengths on Nitrogen Iodide.

In these experiments solutions prepared according to Landolt's directions were used to obtain light belonging to given regions of the spectrum. Two Welsbach incandescent burners were employed as a source of light. The light from these was passed first through a condenser, then through the colored solution, and was finally reflected by a plane mirror on to the surface of crystalline nitrogen iodide mounted on a glass slide in 3N-ammonia. The slide itself was placed on a plane mirror. When light was allowed to fall on the nitrogen iodide decomposition began and, after the saturation of the liquid with nitrogen, bubbles of gas were seen to form on the crystals. It was possible to determine with great accuracy the instant at which these bubbles appeared. The time in seconds from the instant of exposure to light to the first appearance of bubbles was noted. This may be taken as inversely proportional to the intensity of the action of the light, assuming that the same amount of liquid surrounding the crystals is saturated in each case before the bubbles become visible.

When the slide was placed in a photographic dark room no bubbles of gas appeared in twenty minutes. In the diffused daylight which reached the slide in the apparatus, one hundred and eighty seconds elapsed before bubbles were seen.

The following table shows the time of exposure to different kinds of light, in seconds, before bubbles of gas appeared:

	First set of experiments.	Second set of experiments.
White light	14	14
Red "	48	49
Green "	90	92
Blue "	72	70
Indigo "	135	140

These results confirm Guyard's observation that the red end of the spectrum decomposes nitrogen iodide most readily, and that the action gradually becomes less as the wave-length of the light used diminishes. A secondary maximum, however, appears in the blue.

We have to thank Mr. F. F. Blackman, Fellow of St. John's College, Cambridge, for the use of his microscope and solutions, and for very kind assistance in these observations on the action of light.

CHEMICAL LABORATORY, ST. BARTHOLOMEW'S HOSPITAL AND COLLEGE, LONDON.

FORMATION OF INDIGO FROM DIPHENYLDIKETOPIPERAZINE.

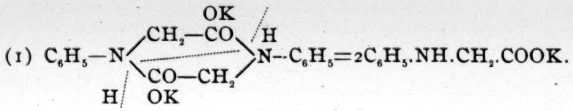
BY M. KUHARA AND M. CHIKASHIGE.

In the course of certain investigations on some complex compounds of the closed carbon-nitrogen nucleus, the authors saw an opportunity to try a new method for the formation of indigo. They believed that the compound diphenyldiketopiperazine, $C_6H_5.N\begin{<}CO—CH_2\\CH_2—CO\end{>}N.C_6H_5$, first prepared by Abenius,[1] would split up on fusing with dry caustic potash into phenylglycocoll, which must instantly change by the further action of the alkali to pseudoindoxyl and finally the latter to indigo by oxygen, the last part of the reactions proceeding analogously to those of Heumann's synthesis.[2] The

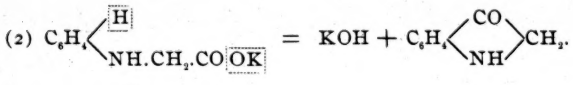
[1] Ber. d. chem. Ges., **21**, 1665. The same compound was prepared by Hausdörfer by heating aniline, chloracetic acid, and sodium acetate, and called by him diphenyl-α-γ-diacipiperazine.—Ber. d. chem. Ges., **22**, 1797.

[2] Ber. d. chem. Ges., **23**, 3043.

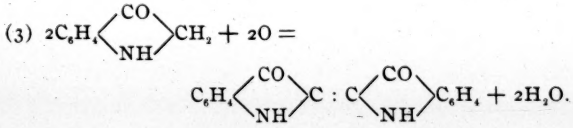
series of reactions which the authors supposed would take place, is represented by the following equations :



(1) $C_6H_5-N(CH_2-CO-OK)(CO-CH_2-OK)(H)(H)N-C_6H_5 = 2C_6H_5.NH.CH_2.COOK.$



(2) $C_6H_4(H)(NH.CH_2.CO.OK) = KOH + C_6H_4(CO)(NH)CH_2.$



(3) $2C_6H_4(CO)(NH)CH_2 + 2O =$

$C_6H_4(CO)(NH)C : C(CO)(NH)C_6H_4 + 2H_2O.$

For the purpose of testing the authors' view, diphenyldiketopiperazine was prepared from monochloracetanilide,

$$CH_2Cl.CO.NH.C_6H_5,$$

according to Abenius' directions, and the compound thus obtained was fused with dry caustic potash, by which process indigo blue was found to be formed, so that we believe that our assumption has been realized.

Experiments.

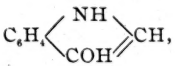
First a large quantity of monochloracetanilide was prepared according to the directions given by P. J. Meyer[1] from monochloracetyl chloride. As Abenius does not give the details of the process for preparing diphenyldiketopiperazine from monochloracetanilide, the authors proceeded in the following way : A molecular quantity of monochloracetanilide was boiled for about five minutes with a molecular quantity of caustic potash dissolved in absolute alcohol. Next, the potassium chloride precipitated was filtered and the alcohol removed from the filtrate by distillation. The residue, which consisted mainly of diphenyldiketopiperazine was washed with hydrochloric acid to remove the aniline formed, and finally dried with ether. The substance was then purified by re-

[1] Ber. d. chem. Ges., **8**, 1152.

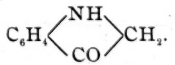
crystallization from alcohol, and the crystals thus obtained were found to melt at 263° as Abenius had observed.

On subjecting a mixture of a certain quantity of diphenyl-diketopiperazine and a little more than an equal quantity of dry, powdered caustic potash in a glass vessel to fusion with sufficient care, the fused mass assumed finally a brownish-yellow color, while at the same time aniline and phenyl isocyanide were formed. The product, dissolved in water, instantly assumed a blue color, and in a short time a blue powder settled upon the bottom of the vessel. The blue coloring-matter, collected and dried, was tested for indigo. It was found to possess all the properties of indigo.

It will be remembered that some years ago Flimm[1] effected the synthesis of indigo by fusing monobromacetanilide, $CH_2Br.CONH.C_6H_5$, with dry caustic potash and subsequently oxidizing the aqueous solution of the product by air. The reactions in his process have, however, remained quite obscure hitherto, but have now, we believe, been made clear by the authors' synthesis. He states: "Indigo wird nicht direct gebildet, sondern als erstes Condensationsprodukt des Monobromacetanilids entsteht Indoxyl,



oder vielleicht ein Pseudoindoxyl der Formel

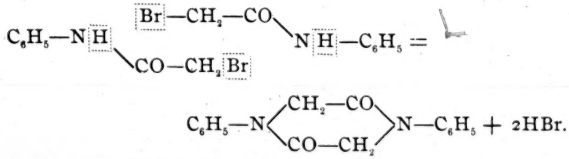


Dieses Zwischenglied geht durch Oxydation in Indigo über. Es ist mir nicht gelungen, dasselbe zu isoliren und rein darzustellen, da es äusserst unbeständig zu sein scheint. Besonders die Entstehung des Pseudoindoxyls hat die grösste Wahrscheinlichkeit für sich. Es tritt dann mit dem Brom ein Wasserstoffatom des Benzolkerns aus. Die Carbonylgruppe tritt an dessen Stelle, nämlich benachbart zum Stickstoff, und zwischen letzterem und der Methylengruppe findet einfache Bindung statt."

[1] Ber. d. chem. Ges. **23**, 57.

Heumann[1] also ventured to explain the nature of the reactions in Flimm's synthesis, and states: "Ehe aus jenem Körper (Monobromacetanilide) indess Pseudoindoxyl oder Indigo entstehen kann, musste zuerst eine Umlagerung zwischen den Gruppen CO und CH_2 erfolgen. Ob hierbei vielleicht als Zwischenprodukt das Bromid des Phenylglycocolls und, da Kali vorhanden ist, hieraus Phenylglycocoll resp. dessen Kaliumsalz entsteht, muss vorerst dahingestellt bleiben."

The explanations, both of Flimm and of Heumann, with regard to the nature of the molecular rearrangement, which consists apparently of the mutual exchange of the positions of the groups CO and CH_2, are unsatisfactory. The authors have, however, found a more probable explanation in supposing that diphenyldiketopiperazine may possibly be formed from monobromacetanilide, as its first condensation-product, on fusing with dry caustic potash, the action of which is considered to be analogous to that of alcoholic potash, and that, as in the authors' synthesis, it may instantly split up into phenylglycocoll which is, in turn, transformed into pseudoindoxyl and this into indigo. The formation of diphenyldiketopiperazine from monobromacetanilide by the action of dry caustic potash is represented thus:



CHEM. LABORATORY, THE IMP. UNIVERSITY, KYOTO, JAPAN, March 24, 1900.

[1] Ber. d. chem. Ges., **23**, 3045.

THE ACTION OF NITRIC ACID ON VANILLIN.

By William B. Bentley.

INTRODUCTION.

The investigation of this subject was undertaken in consequence of some unsuccessful attempts to oxidize the chlorvanillin prepared by A. E. Menke, to chlorvanillic acid. It was hoped that by regulating the action of dilute nitric acid it might be found possible to convert vanillin and its substitution-products into corresponding vanillic acids. The purpose of the experiment was entirely defeated by the unexpected action of dilute nitric acid. The reaction which apparently occurred first was an oxidation identical with that observed by Tiemann[1] when vanillin was boiled with a solution of ferric chloride, whereby a substance $(C_6H_2CHO.OCH_3.OH)_2$, by him called dehydrodivanillin, was produced. Concurrently with this reaction, but proceeding more slowly, was a substitution of a nitro group in the ring. This action was rather surprising, as the nitration took place even when the strength of the nitric acid did not exceed 5 per cent. In addition to these two compounds, perhaps by subsequent action of the nitric acid on nitrovanillin, dinitroguaiacol was formed and in minute quantity another compound, the identity of which it was impossible to determine.

Nitrovanillin was converted into dinitroguaiacol by further action of nitric acid and its constitution thus shown to be

$$C_6H_2.CHO.OCH_3.OH.NO_2(CHO : OCH_3 : OH : NO_2 = 1 : 3 : 4 : 5).$$

The position of the hydrogen in the vanillin molecule which is most easily substituted is therefore in the meta relation to the aldehyde and oxymethyl groups, and ortho to the hydroxyl group. Nitrovanillin was also oxidized to nitrovanillic acid, a compound previously described by Weselsky and Benedikt.[2] Attempts were made to obtain amidovanillin but, although the compound was obtained as a flocculent white precipitate, it blackened immediately, and all efforts to obtain

[1] Ber. d. chem. Ges., 18, 3493.
[2] Monatsh. Chem., 3, 392.

it in pure condition failed. Various experiments were made with a view to carrying the nitrovanillin by reduction and subsequent treatment by the Sandmeyer reaction to chlorvanillin, but they were unsuccessful. The organic compound seemed to be entirely lost in the process.

EXPERIMENTAL PART.

Nitrovanillin.

Vanillin in lots of about 2 grams each was dissolved in water by warming 1 part of vanillin with 80 of water. To this solution was added 8 parts by volume of common strong nitric acid, sp. gr. 1.38. The mixture was digested at 50°, which caused a strong yellow color to be developed in the solution, accompanied presently by the separation of a dirty white precipitate, the color of which became rapidly darker. In one experiment the precipitate was filtered out as soon as any considerable quantity had accumulated. After further digestion another precipitate appeared, and this was separated by filtration, after which the digestion was continued until precipitation was at an end. The entire period was about two hours. The first portion was found to consist of about 80 per cent dehydrodivanillin, while the second was 30 per cent, and the last portion, which was about two-thirds of the whole precipitate, contained but 10 per cent dehydrodivanillin. The results show that, although the formation of nitrovanillin begins immediately, the greater part of this compound appeared only after some time while dehydrodivanillin was formed almost entirely at the very outset. The yield of nitrovanillin in this reaction was about 50 per cent of the weight of vanillin taken, while that of dehydrodivanillin was about 20 per cent. The precipitate was washed once or twice with water, but this treatment should not be carried too far as nitrovanillin is somewhat soluble in water. The residue is next extracted with boiling alcohol until the extract is no longer yellow. This extraction can be made much quicker by substituting boiling glacial acetic acid for alcohol, as the compound is freely soluble in hot acetic acid but only fairly soluble in alcohol. The nitrovanillin was recrystallized from alcohol or

acetic acid until it showed the constant melting-point, 176°.

The introduction of a nitro group by nitric acid of so great dilution seemed so unusual that the compound was prepared by a more general method. Vanillin was dissolved in glacial acetic acid and an acetic acid solution of the calculated quantity of fuming nitric acid was added. The mixture became very red and almost immediately precipitated nitrovanillin in amount only slightly less than theory demands. This compound was essentially pure, as it was shown that by recrystallization its melting-point was very little changed. The substance so obtained is identical in every respect with that prepared with dilute acid, as before described.

In the analysis of this compound the ordinary combustion methods did not succeed, although repeated trials were made and all possible precautions were observed. The identity of the compound was so unmistakably indicated by the methods of preparation that this evidence, together with some determinations of nitrogen by the Kjeldahl method and analytical results with the potassium salt as described below, were taken as sufficient proof of its composition.

I. 0.9961 gram of the substance dissolved in sulphuric acid, reduced with sodium thiosulphate, and treated according to the method of Kjeldahl, yielded ammonia sufficient to neutralize 47.31 cc. decinormal acid.

II. 1.0197 grams of substance treated as above yielded ammonia sufficient to neutralize 47.78 cc. decinormal acid.

III. 1.1146 grams of substance yielded ammonia sufficient to neutralize 53.66 cc. decinormal acid.

	Calculated for $C_6H_3CHO.OCH_3.OH.NO_2$.	Found. I.	II.	III.
N	7.11	6.65	6.56	6.74

As results obtained by this method are usually low when nitrogen is present in the oxidized condition these results seem admissible.

Nitrovanillin, in the pure state, melts at 176° and crystallizes best from glacial acetic acid in which it dissolves freely when hot and but slightly when cold. It is less soluble in hot alcohol, from which it separates, on cooling, in crystals similar to those from acetic acid, only smaller and more poorly

defined. The crystals are pale yellow plates, apparently of the hexagonal system. The solution gives a yellow stain somewhat similar to that of picric acid. In methyl alcohol it is somewhat more soluble than in ethyl. It is soluble in chloroform and carbonic disulphide. It dissolves but little in acetone, is practically insoluble in ether. It dissolves to a limited extent in water and in hydrochloric and sulphuric acids. With nitric acid it gives dinitroguaiacol as described below. Nitrovanillin probably forms salts with all the basic elements. It is sufficiently acid to dissolve calcium carbonate, forming the yellow calcium salt. Solutions of salts of the basic elements were tested with a cold saturated solution of the potassium salt. In most cases a yellow precipitate was produced, which precipitate dissolved if the solution was heated. In the following cases no precipitate was produced, owing, probably, to the solubility of the salts which would have been formed: The salts of the alkalies, magnesium, manganese, cobalt, nickel, mercury. Chromium formed a light-green precipitate, copper a greenish-yellow, and lead a voluminous yellow precipitate which seemed only slightly soluble in hot water. The substance is not liberated from its alkaline salts by carbon dioxide nor by sulphuretted hydrogen but is precipitated by acetic acid.

Potassium Salt of Nitrovanillin.—To establish further the identity of the nitrovanillin the potassium salt was prepared by dissolving nitrovanillin in dilute potassium hydrate by the aid of heat. As the salt dissolves easily in hot water and but little in cold, the compound was easily purified. It was dried at 100° and analyzed by dissolving in water, precipitating the organic matter with sulphuric acid, and evaporating the solution of potassium sulphate which had been filtered from nitrovanillin.

I. 0.2465 gram of the salt gave, when treated as above, 0.0907 gram of potassium sulphate.

II. 0.4090 gram of the salt gave 0.1516 gram potassium sulphate.

	Calculated for $C_6H_2CHO.OCH_3.OK.NO_2$.	Found. I.	II.
K	16.63	16.52	16.64

It was observed that in drying the crystals they underwent considerable change in appearance, which seemed to indicate that they originally contained water of crystallization. To determine the amount of this water a freshly crystallized specimen was dried with filter-paper and then exposed in air for two hours. The crystal water was driven off in the steam oven. Although satisfactory results could not be secured because water was slowly lost at ordinary temperature, and on account of the nature of the crystal mass, perfect removal of adhering water did not seem to be effected by pressing with filter-paper. The following results leave but little doubt, however, that there was a single molecule of crystal water.

I. 1.0788 grams of the crystals, dried at the temperature of the steam oven, lost 0.0721 gram.

II. 1.3178 grams of crystals lost 0.0878 gram.

	Calculated for $(C_6H_3CHO.OCH_3.OK.NO_2)H_2O$.	Found. I.	II.
H_2O	7.11	6.68	6.66

The potassium salt of nitrovanillin separates from its hot aqueous solution in a compact mass of long fibrous crystals. These are of an extremely bright orange-red color when hydrous, but on losing water they become a darker red. The salt dissolves freely in hot water and much less in cold, and its solubility is much decreased by the presence of potassic hydrate. It dissolves quite readily in hot ethyl alcohol and only slightly in cold. In methyl alcohol it is more soluble than in ethyl when cold, and is not separated from this solvent when the hot solution is cooled. It is slightly soluble in acetone, very slightly in ether, and insoluble in benzol and chloroform.

Dehydrodivanillin.

The writer is unable to present analytical proof that the insoluble compound obtained, as above described, is dehydrodivanillin, because no means of obtaining satisfactory results were found, although much time was spent in the effort. As the compound is insoluble in all common organic solvents the attempt was made to purify it by dissolving in potassic hydrate and precipitating with carbon dioxide. This process

was repeated many times, but as it melts above 300° there was no proof of the purity of the samples analyzed and the results seem to show that this method was not sufficient. That the compound was really dehydrodivanillin it seems there is little doubt. In the first place, the method of preparation was similar to that of Tiemann,[1] the very dilute nitric acid replacing aqueous ferric chloride as an oxidizing agent. In the second place, the compound melts above 390°, and has in every other respect the somewhat unusual properties of dehydrodivanillin. It was compared with the compound made by action of aqueous ferric chloride and no difference between the two samples was observed. Some efforts were made to prepare and analyze the sodium salt. The compound was boiled with an insufficient quantity of an alcoholic solution of sodic ethylate, and the unaltered compound filtered out. The solution of the sodium salt was then evaporated, and the salt separated either by crystallization or by complete evaporation. In one determination of sodium the percentage found was in close agreement with that calculated for the disodium salt of dehydrodivanillin, but this result had to be rejected as untrustworthy because subsequent determinations gave too low results, indicating that the disodium salt contained also some of the monosodium salt. As there seemed to be no way of obtaining the disodium salt in a condition of purity the subject was abandoned.

The Action of Nitric Acid on Nitrovanillin.

The dilute nitric acid mother-liquor from which the nitrovanillin was filtered, as described above, had a strong yellow color showing that some compound soluble in water was also formed. The isolation of this compound proved rather troublesome. When the large volume of water in which it was dissolved was evaporated by heat, the nitric acid remaining, oxidized the organic matter to oxalic acid. An ineffectual attempt was made to prevent this by reducing the nitric acid with alcohol. A more satisfactory result was secured by neutralizing the liquid with potassic hydrate and evaporating the neutral solution to dryness. The separation of the potassium

[1] Ber. d. chem. Ges., 18, 3493.

nitrate from the potassium salt of the organic compound was, however, a matter of no little difficulty as the two salts crystallized together, being apparently isomorphous. It was indeed found impossible in this way to obtain any considerable quantity of the compound, though a small amount was obtained by the following method: The dry residue was repeatedly extracted with strong alcohol, which dissolved most of the organic salt and considerable quantities of the nitrate. The alcoholic solution was then freed from potassium by precipitation with dilute sulphuric acid. In this way enough of the compound was secured to show that it melted at 123°, and was probably the dinitroguaiacol prepared by Hertzig.[1] Fortunately, it was found that if the action of nitric acid on vanillin was managed in a manner differing somewhat from the one described above, the compound could be obtained without much trouble. The vanillin was dissolved in water as before, but the volume of water was doubled so that the solution could be cooled without the separation of vanillin. After cooling, the nitric acid was added and the mixture was digested in the cold for several days. The products were the same as before, except that the dinitroguaiacol was found in greater quantity, probably on account of the conversion of nitrovanillin to dinitroguaiacol by more prolonged action of nitric acid. The dehydrodivanillin was in this process precipitated in a slimy condition, which rendered the extraction of the nitrovanillin difficult. After separating the precipitated matter, the acid liquid was allowed to evaporate spontaneously, when the dinitroguaiacol separated out in some quantity. It was recrystallized from dilute alcohol until it showed the constant melting-point 123°. To be sure of its identity it was analyzed with the following result:

0.1783 gram of the substance gave, on combustion, 20.9 cc. nitrogen measured at 20° and 727 mm. pressure.

	Calculated for $C_6H_2(NO_2)_2OCH_3OH$.	Found.
N	13.08	12.81

It was also shown that dinitroguaiacol can be made from nitrovanillin by the action of nitric acid, and there seems no

[1] Monatsh. Chem., **3**, 825.

reason to think that the dinitroguaiacol obtained by the action of nitric acid on vanillin was not the product of a second reaction between the nitric acid and the nitrovanillin first formed. Nitrovanillin was warmed with water containing a little acetic acid to promote solubility and 2 or 3 molecules of nitric acid were added for each molecule of nitrovanillin present. On cooling, dinitroguaiacol separated out and was recognized by its melting-point and other properties. The quantity obtained in this process was about one-half the nitrovanillin used.

The conversion of nitrovanillin into dinitroguaiacol determines the structure of nitrovanillin for Hertzigs,[1] reasoning by analogy between the behavior of triamidophenol and that of diamidoguaiacol (obtained by reduction of dinitroguaiacol), concludes that dinitroguaiacol has the structure.

$C_6H_2(NO_2)_2OCH_3OH(NO_2 : OCH_3 : OH : NO_2 = 1 : 3 : 4 : 5)$.

This makes it evident that the NO_2 group standing at 5 was the one in nitrovanillin, while the other had displaced the CHO group of nitrovanillin when this latter compound was acted upon by nitric acid. The constitution of nitrovanillin is therefore

$$C_6H_2CHOOCH_3OHNO_2(CHO : OCH_3 : OH : NO_2 = 1 : 3 : 4 : 5).$$

In neutralizing the nitric acid for the purpose of obtaining the dinitroguaiacol by the method mentioned above, it was observed that a slight excess of alkali caused the liquid to become a deep blood-red. Attempts were made to isolate the substance which gave this reaction by precipitating with acetate of lead. By this process a rather voluminous brown precipitate was produced and the blood-red color entirely disappeared, leaving the solution orange-red, the color of the potassium salt of dinitroguaiacol. Although this precipitate was repeatedly collected and treated with sulphuretted hydrogen no organic product was ever obtained.

Oxidation of Nitrovanillin.

In the earlier attempts to oxidize nitrovanillin, very unsat-

[1] Monatsh. Chem., **3**, 825.

isfactory results were obtained, because an excess of the oxidizing agent, alkaline permanganate, effected the complete destruction of the molecule. No means was found of judging from the color of the solution when the oxidation had proceeded far enough. The desired amount of oxidation was finally obtained by using a measured volume of roughly standardized permanganate solution. The oxidizing power of the permanganate was determined by titrating against an acid solution of ammonio-ferrous sulphate and allowing that the oxidizing power in alkaline solution was three-fifths that in acid solution. By this means it was estimated that 1 gram of nitrovanillin required $33\frac{1}{3}$ cc. of permanganate solution saturated at ordinary temperature. The process was conducted as follows: 2 grams of nitrovanillin were dissolved in a slight excess of potassic hydrate. To this solution were added 80 cc. of the permanganate solution, and the mixture was digested at ordinary temperature. The red color of the nitrovanillin salt was obscured by the purple of the permanganate which presently became green and finally yellow. The mixture was then heated to prevent any of the potassium salt of nitrovanillic acid from remaining enclosed in the precipitate of oxides of manganese, and the latter substance was filtered out. The yellow solution thus obtained was acidified with sulphuric acid which precipitated a portion of the organic matter, and the remainder was extracted with ether. It was found impossible to obtain anything by evaporation, as the nitrovanillic acid was either volatilized with steam or more likely decomposed by the hot acid. The product obtained, in spite of the excess of permanganate used, contained a considerable quantity of unaltered nitrovanillin, from which it was found difficult to separate it by crystallization. Fortunately, nitrovanillic acid is very readily soluble in ether, while nitrovanillin is almost insoluble in this solvent. The crude product which melted at about 190° was therefore treated with ether, and the soluble part further purified by recrystallization, while the soluble portion was again oxidized. As a crystallizing medium, dilute alcohol, which was first used, proved unsatisfactory, as the compound separated in very poor crystals and their appearance was no criterion of their purity.

The compound crystallized well from glacial acetic acid, and the compound was readily purified by use of this solvent. The pure compound melted at 216°–216°.5. Its identity was confirmed by the following analyses:

I. 0.1833 gram of the substance gave, on combustion, 0.0653 gram H_2O, and 0.3012 gram CO_2.

II. 0.1359 gram of the substance gave, on combustion, 0.0518 gram H_2O, and 0.2242 gram CO_2.

III. 0.1826 gram of the substance gave, on combustion, 11.73 cc of N at 20°.5 and 730.85 mm. pressure.

	Calculated for $C_6H_2CO_2HOCH_3OHNO_2$.	Found. I.	II.	III.
C	45.07	44.81	44.99	....
H	3.29	3.96	4.23	....
N	6.57	....	....	7.04

This compound, which must have the constitution

$$C_6H_2CO_2HOCH_3OHNO_2(CO_2H : OCH_3 : OH : NO_2 = 1 : 3 : 4 : 5),$$

seems to differ in its properties from the nitrovanillic acid described by Weselsky and Benedikt[1] only in its melting-point, their compound melting at 202° instead of 216°.

The difficulties encountered in the preparation of pure nitrovanillic acid suggest a possible explanation of the low melting-point obtained by Weselsky and Benedikt. As their compound was made by oxidation of nitroeugenol with permanganate, nitrovanillin was in all probability an intermediate product. The experiments made by the writer show in the first place that it is improbable that the oxidation was carried to such a point that all the nitrovanillin was converted to the acid. In the second place, it is difficult, if not impossible, to separate nitrovanillic acid from nitrovanillin by crystallization. The probability seems to be that their compound contained a trace of nitrovanillin. By nitration of acetylvanillic acid and subsequent saponification Tiemann and Matsmoto[2] obtained a nitrovanillin in which the nitro group occupied the ortho position with reference to the carboxyl instead of the meta position as it does here. It is perhaps in-

[1] Monatsh. Chem., 3, 392.
[2] Ber. d. chem. Ges., 9, 944.

teresting to note that the nitro group enters vanillin and eugenol at a point different from that which it enters in acetylvanillic acid. That this difference is due to the influence of the acetyl group is proved by the fact that Pschorr and Sumuhann,[1] by action of nitric acid on acetylvanillin, got a nitro derivative which yields nitrovanillin of the constitution

$$C_6H_2CHOOCH_3OHNO_2(CHO : NO_2 : OCH_3 : OH = 1 : 2 : 3 : 4).$$

For the sake of possible comparison the writer adds the properties of the compound as he observed them. Nitrovanillic acid crystallizes from dilute alcohol in small, yellow needles, from acetic acid in well developed plates belonging apparently to the monoclinic system. It is quite soluble in cold ethyl or methyl alcohol; also in acetone or ether; soluble in hot glacial acetic acid; very sparingly in cold; it dissolves slightly in water or chloroform, very slightly in carbon disulphide; it dissolves in sulphuric or nitric acid and is decomposed by the latter. Hydrochloric acid has apparently no action on it. The crystals from acetic acid are light-yellow and transparent, and contain acetic acid. The acetic acid is readily lost and the crystals fall to a powder, which is much darker than the crystals. An effort was made to determine the acetic acid in these crystals. As acetic acid is lost at ordinary temperature, the results were not wholly satisfactory. The substance was crystallized, dried between filter-papers, and the acetic acid determined by heating in the steam oven. The results were as follows:

I. 0.9618 gram of the crystals lost 0.2794 gram, or 29.05 per cent.

II. 0.5506 gram of the crystals lost 0.1610 gram, or 29.23 per cent.

One molecule of acetic acid would require 21.98 per cent, while 1.5 molecules require 29.70 per cent. The results seem to indicate fairly well that the crystals obtained from an acetic acid solution of nitrovanillic acid have the composition

$$C_6H_2CO_2HOCH_3OHNO_2 1\tfrac{1}{2}CH_3CO_2H.$$

[1] Ber. d. chem. Ges., **32**, 3405.

ON THE EFFECT OF OXIDIZING AGENTS ON THE REDUCTION OF MERCURIC CHLORIDE BY OXALIC ACID.

By J. H. Kastle and W. A. Beatty.

It has been shown by Amato[1] and also in this laboratory[2] that the chemical effect of light is exerted only above certain temperatures, or better, perhaps, between certain rather narrow limits of temperature. In seeking for another reaction on which to test this point, it occurred to one of us (Kastle) that perhaps Eder's chemical photometer, which depends on the reduction of mercuric chloride by ammonium oxalate in the sunlight, and which is influenced to a considerable extent by temperature, might furnish a chemical reaction well suited for our purpose.[3]

In attempting to follow the progress of this reaction by determining by means of potassium permanganate the quantity of oxalate remaining unaltered, it was observed that a very rapid reduction of the mercuric chloride occurred on adding even a few drops of the solution of permanganate. In fact, it soon became apparent that it would be impossible to measure the rate of change in this way. The accelerating effect of the permanganate on the progress of the reaction proved to be so remarkable and interesting that the problem of measuring the effect of light on the reaction at different temperatures was temporarily abandoned in order that the acceleration produced by the permanganate and other oxidizing agents might be more thoroughly studied. In what follows, unless expressly stated to the contrary, solutions of ammonium oxalate and mercuric chloride of the following concentrations were employed: 40 grams of ammonium oxalate per liter, and 50 grams of mercuric chloride per liter.

In our experiments these solutions were mixed immediately before using in the proportion of two volumes of the oxalate solution to one volume of the chloride. Unless stated to the contrary, 10 cc. of the oxalate with 5 cc. of the chloride solu-

[1] Gazz. chim. Ital., **14**, 57.
[2] This Journal, **20**, 159-163; J. Am. Chem. Soc., **21**, 268-272.
[3] Ber. d. chem. Ges. **13**, 166.

tion were employed in each experiment. The experiments were conducted in thin-wall color-tubes, similar in shape to nesslerizing cylinders. In order to determine something as to the extent of the acceleration produced by potassium permanganate on the reaction, the following experiment was tried:

Two tubes were prepared: each of these containing 10 cc. of ammonium oxalate, together with 5 cc. of mercuric chloride. To one of them 1 drop of a N/100 solution of potassium permanganate was added. The two tubes were then placed side by side in the direct sunlight and allowed to remain thus exposed for ten minutes. At the end of this time they were removed from the direct sunlight and quickly filtered. The precipitates of mercurous chloride thus obtained were heated with 10 cc. of caustic potash solution and 0.5 gram of zinc dust. The two solutions were then filtered through asbestos and the filtrates titrated with N/10 silver nitrate. In this way the amount of mercurous chloride precipitated in each of the two tubes was determined. In the tube to which 1 drop of N/100 permanganate had been added, 28.2 per cent of the mercuric chloride had been reduced; whereas, in the tube to which no permanganate had been added, only 3.48 per cent of mercuric chloride had been reduced. Thus, it was shown that about 0.016 mgm. of potassium permanganate in 15 cc. of solution was sufficient to produce a reduction of mercuric chloride by ammonium oxalate eight times faster than when the oxalate and mercuric chloride were allowed to react alone. In order to make sure that only mercuric chloride was precipitated in the presence of the permanganate, some of the precipitate thus obtained was dried and the chlorine in it determined with the following result:

	Calculated for HgCl.	Found.
Cl	15.04	15.16

The attempt was then made to determine the smallest quantity of potassium permanganate capable of producing an acceleration of the reaction. This was accomplished in the following manner:

A number of tubes were prepared containing 10 cc. of am-

monium oxalate together with 5 cc. of mercuric chloride. Two of these tubes were then placed in the direct sunlight, and to one of them 1 drop of a solution of potassium permanganate of known strength was added. The time required for the formation of the precipitate of mercurous chloride, together with the quantity of the precipitate produced in each tube in a given time, afforded a rapid, though rough, method of measuring the acceleration produced. The following is a summary of the results obtained :

1 drop of N/100 $KMnO_4$[1] = 0.00001578 gram $KMnO_4$ greatly accelerated the reduction.

1 drop of N/2500 $KMnO_4$ = 0.00000063 gram $KMnO_4$ greatly accelerated the reduction.

1 drop of N/20000 $KMnO_4$ = 0.000000078 gram $KMnO_4$ considerably accelerated the reduction.

1 drop of N/40000 $KMnO_4$ = 0.000000039 gram $KMnO_4$ very perceptibly accelerated the reduction.

1 drop of N/80000 $KMnO_4$ = 0.0000000195 gram $KMnO_4$ slight but perfectly perceptible acceleration.

1 drop of N/160000 $KMnO_4$ = 0.00000000975 gram $KMnO_4$, very slight acceleration.

It will be seen, therefore, that about 0.00000000975 gram of $KMnO_4$, in 15 cc. of solution, is about the smallest quantity of this substance capable of accelerating the reduction of mercuric chloride by ammonium oxalate under the most favorable conditions.

The acceleration by permanganate was found to be greatest in direct sunlight. In diffused light and in gaslight, however, it was still very marked, but in the dark the accelerating effect of the permanganate was observed to be very much impaired. Results similar to the above were obtained with a mixture of potassium permanganate and sulphuric acid. In this case, however, the acceleration was not quite so pronounced in certain of the experiments, indicating that the free sulphuric acid exerted a retarding action on the reduction. Other acids, such as hydrochloric and nitric, were also found to retard the reduction to a noticeable extent.

[1] The concentration of the solution of permanganate is based upon that of a decinormal solution of this salt, containing 3.156 grams per liter.

Ferric chloride was also found to accelerate the reduction in direct sunlight, as may be seen from the following:

1 drop of N/100 $FeCl_3$ = 0.00008125 gram $FeCl_3$ in 15 cc. solution, caused great acceleration.

1 drop of N/2000 $FeCl_3$ = 0.000004062 gram $FeCl_3$ in 15 cc. solution, produced great acceleration.

1 drop of N/4000 $FeCl_3$ = 0.000002031 gram $FeCl_3$ in 15 cc. solution, acceleration plainly perceptible.

1 drop of N/8000 $FeCl_3$ = 0.000001016 gram $FeCl_3$ in 15 cc. of solution, very slight acceleration.

About 0.001 mgm. of ferric chloride in 15 cc. solution is therefore believed to be the smallest quantity of this substance that can cause acceleration under the most favorable conditions. Still other oxidizing agents were found to greatly accelerate the reduction of mercuric chloride by ammonium oxalate in the sunlight. Among them may be mentioned the following: Iron alum, auric chloride, platinic chloride, thallic chloride, chrome alum, uranium nitrate, iodic acid, potassium bromate, ammonium persulphate, chlorine water, etc. On the other hand, a few of them such as chromic acid, potassium chromate, and dichromate, were found to retard the change.

Reduction of Thallic Chloride by Ammonium Oxalate in the Sunlight.

Thallic chloride is rapidly reduced by ammonium oxalate in the sunlight with the formation of thallous chloride, ammonium chloride, and carbon dioxide:

$$TlCl_3 + (NH_4)_2C_2O_4 = TlCl + 2NH_4Cl + 2CO_2.$$

This reaction is altogether analogous to the reduction of mercuric chloride by ammonium oxalate, and like the latter it has been found to be greatly accelerated by other oxidizing agents. A solution of thallic chloride was prepared containing 87.2 grams $TlCl_3$ per liter. Several tubes were then prepared containing 10 cc. of the solution of ammonium oxalate (40 grams of ammonium oxalate per liter) and 5 cc. of the thallic chloride solution. One of these tubes was placed in diffused light and a second one in the direct sunlight. The reduction

in both cases was considerable. In the tube exposed to direct sunlight, however, it was greatly in excess of that in the diffused light. Two tubes containing a mixture of thallic chloride and ammonium oxalate were placed in the direct sunlight and a drop of N/20 ferric chloride added to one of them. The most remarkable acceleration in the reduction of the thallic chloride was thus brought about. In the same way, 1 drop of N/100 potassium permanganate was observed greatly to accelerate the reduction.

While certainly very remarkable, these are by no means the only instances in which oxidation or reduction is greatly accelerated by the presence of other substances, usually oxidizing agents, and not immediately concerned in the change. According to Harcourt[1] chromic acid only oxidizes oxalic acid in the cold in the presence of manganous sulphate. Lothar Meyer[2] and others have found that the oxidation of solutions of sulphur dioxide in water by the oxygen of the air is greatly accelerated by certain metallic salts, such as the sulphates of manganese, copper, iron, and cobalt. Jorissen[3] has shown that boric and sulphuric acids increase the velocity of oxidation of oxalic acid in the light. He made the further interesting observation in this connection that while manganese sulphate promotes the oxidation of oxalic acid in the dark, it actually acts as a preservative of it in the light. Quite recently, Jorissen and Reicher[4] have shown that in diffused light the oxidation of oxalic acid is accelerated by the sulphates of iron, chromium, cerium, thorium, and erbium; also by sodium fluoride, and by manganese sulphate, acetate, butyrate, benzoate, and oxalate.

On the other hand, potassium, magnesium, and yttrium sulphates exert no accelerating influence on the oxidation. In sunlight manganese oxalate, sulphate, acetate, butyrate, and benzoate increased the rate of oxidation. According to these observers, the acceleration depends on the nature of the catalytic agent, and increases with its concentration. Further, the acceleration produced by manganese salts cannot be ac-

[1] British Association, 34th Meeting, 1864.
[2] Ber. d. chem. Ges., **20**, 3058.
[3] Ztschr. angew. Chem. (1899), 521–525.
[4] Ztschr. phys. Chem. (1899), **31**, 142–163.

counted for by the formation of manganese oxalate, for the reason that this substance is more slowly oxidized than oxalic acid itself. Richardson[1] has made the interesting observation that in the sunlight and in the presence of an excess of oxygen, hydrogen peroxide is produced in the oxidation of oxalic acid.[2] He also found that hydrogen peroxide accelerates the oxidation of oxalic acid by oxygen gas in the light. In view of the great diversity of these phenomena, it is not an easy matter to frame an hypothesis as to the cause of the acceleration of such oxidations which would be applicable to all cases. Perhaps the best explanation that can be given of such processes at present is that advanced by Lothar Meyer[3] to account for the accelerating influence of such salts as manganous sulphate on the oxidation of sulphurous acid by gaseous oxygen. According to him, the salt causing the acceleration simply acts as a carrier of oxygen, and the part played by such salts is quite analogous to that taken by such substances as ferric chloride and other chlorine carriers in processes of substitution. In the same way, the part played by other oxidizing agents, such as potassium permanganate, ferric chloride, and thallic chloride in accelerating the oxidation of ammonium oxalate by mercuric chloride in the sunlight might also be explained. When ferric chloride, for example, is added to a solution of ammonium oxalate and mercuric chloride, it seems probable, at least, that the following changes would occur :

1. Reduction of ferric chloride to ferrous chloride by the ammonium oxalate.

2. Oxidation of the ferrous chloride to ferric chloride by the mercuric chloride.

3. Oxidation of the ammonium oxalate by the mercuric chloride.

It has been shown in most cases, at least, that the substances causing the acceleration of the change under discus-

[1] J. Chem. Soc. (London), **65**, 467 (1894).

[2] Manchot has recently observed the formation of hydrogen peroxide in the oxidation of such substances as oxanthrol in alkaline solutions by atmospheric oxygen. —J. Chem. Soc. (London), May (1900), 300. And still more recently Engler has proved the formation of hydrogen peroxide in a large number of oxidations.—Ber. d. chem. Ges., **33**, 1090.

[3] Ber. d. chem. Ges., **20**, 3058.

sion are themselves capable of being reduced by the ammonium oxalate. It should be noticed in this connection, however, that at certain concentrations ferrous chloride is not oxidized by mercuric chloride, even in the sunlight. The impossibility of such a reaction, however, does not necessarily preclude the idea that this substance may act as a carrier of oxygen in the reduction of mercuric chloride by ammonium oxalate. In solution with ammonium oxalate, mercuric chloride must be in an extremely unstable state. It is therefore conceivable that in this condition it might be easily reduced by a substance altogether incapable of reducing it in its pure aqueous solutions. Or, looked at from a slightly different standpoint, the reducing agents produced in the reaction, such as ferrous chloride, etc., although incapable of reducing mercuric chloride directly themselves, might render it more unstable by their presence, and hence more readily reducible by the ammonium oxalate.

Quite recently, in fact since the above was written, one of us (Kastle) has succeeded in showing by means of the titanic acid reaction, that hydrogen peroxide is produced in small quantities, at least, in the oxidation of oxalic acid by potassium permanganate in the sunlight. As to just what bearing, if any, this observation may have on this problem here under discussion remains to be seen.

STATE COLLEGE OF KENTUCKY,
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